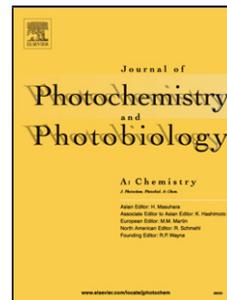


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Perylenebisimide-Fullerene Dyads as Heavy Atom Free Triplet Photosensitizers with Unique Singlet Oxygen Generation Efficiencies

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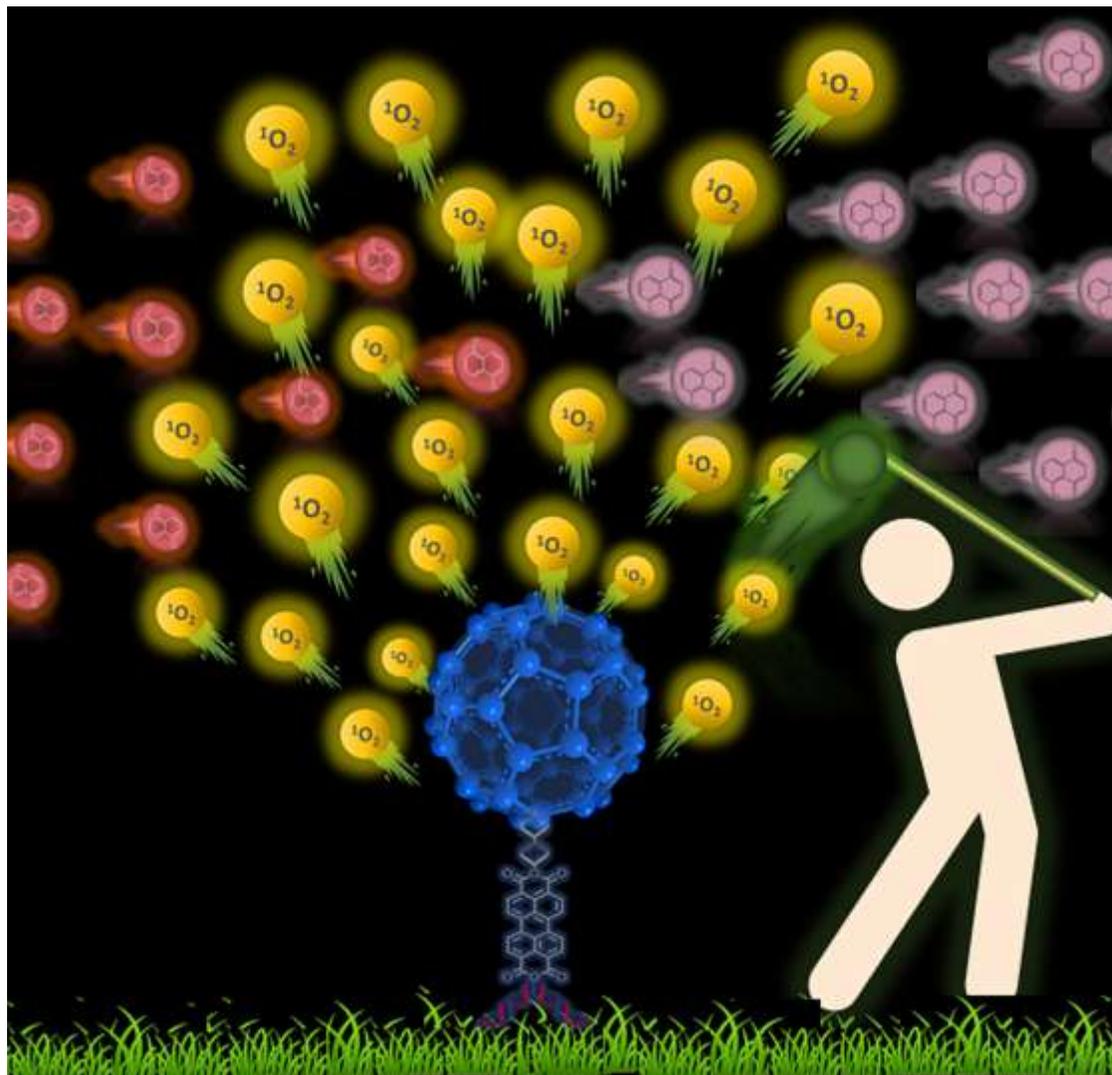
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Graphical abstract



Highlights

- Synthesis of Perylenebisimide-fullerene triads
- Investigation of spectral properties
- Generation of singlet oxygen
- Photooxidation of 1,5-dihydroxynaphthalene

Abstract

We report the synthesis, characterization, photophysical and photochemical properties of two novel perylenebisimide -fullerene dyads (**7** and **8**) bearing one or two perylenebisimide (PBI) units as light harvester and a fullerene as spin converter. The molecular structures of all synthesized compounds were elucidated by mass spectrometry, ^1H and ^{13}C NMR techniques. Their optical properties were investigated by UV-Vis absorption and 2D/3D fluorescence emission spectroscopies. The photochemical studies via direct and indirect method endorsed PBI-fullerene dyads (**7** and **8**) as efficient heavy atom free triplet photosensitizers whereas perylene derivatives did not exhibit any singlet oxygen production. The PBI-fullerene dyads exhibit excellent singlet oxygen quantum yields of 0.93 and 0.95. The PBI-fullerene dyads (**7** and **8**) are also able to use in the photooxidation of 1,5-dihydroxynaphthalene (DHN) to produce juglone and are recognized as stronger than MB as conventional triplet photosensitizers.

Keywords: perylenebisimide, fullerene, singlet oxygen, photochemistry, sensitizers, UV/Vis spectroscopy

1. Introduction

Triplet photosensitizers are not only within the interest field of chemistry but also related with other disciplines owing to various different application areas like photocatalytic reactions [1-3], photovoltaics [4], triplet-triplet annihilation [5] and photodynamic therapy [6, 7]. The common aspect of all these reactions is to generate long-lived triplet excited state of the photosensitizer that is enough to react with molecular oxygen [8]. Designing triplet photosensitizers possessing properties such as strong absorption of visible light, effective intersystem crossing (ISC) and long-lived triplet excited state is essential. The challenge in designing a triplet photosensitizer is to ensure that the triplet excited state is maintained via ISC. Transition metal complexes, Pt^{II}, Ir^{III}, Ru^{II} and bromine/iodine substituted organic dyes (chromophores), are commonly used as triplet photosensitizer [9, 10]. However, heavy atoms could not always provide the ISC or alterations on organic chromophores' chemical structure could vanish the ISC of a known triplet PS [11]. Therefore, it is a requirement to design triplet PSs having predictable ISC without heavy atoms. Hence, multimodular systems can be constructed as heavy atom free triplet photosensitizers bearing energy acceptor fragment like fullerene with genuine intersystem crossing yield and light-harvesting antennae as energy donor [12]. However, designing dyad systems which provide effective triplet excited state is a challenge, yet at this point fullerene-C₆₀ outstands as spin convertor [13]. The intersystem crossing aptitude of the fullerene ($\Phi_{ISC}=1$) is specially intriguing [14], where C₆₀ has been studied for more than a quarter of a century thanks to the Kroto *et al.*, who constitutes an important landmark for the chemistry [15], whereas the triplet photosensitization of fullerene have been stayed raw. The research on this phenomenon commenced with the advent of functionalization techniques by using visible light harvesting chromophores and provided the much-needed stimulus in the field of generation of singlet oxygen and use its triplet energy in the photooxidation reactions [16]. Several organic chromophore-C₆₀ dyads and triads were prepared and applied photocatalysis organic reactions [17, 18]. A few dyads based on perylene and C₆₀ units have been prepared where perylene unit act as NIR light absorbing antenna [16, 19]. Hoffmann *et. al.* reported a ~500 nm light harvesting perylenebisimide-fullerene (PBI-fullerene) dyad and investigated the photophysical processes which possess efficient transfer of the electronic excitation energy from PBI to the fullerene followed by a back-transfer to the perylene unit [20]. This empowered us to explore the singlet

oxygen efficiencies of these dyad systems in the raw regions of the solar spectrum and be able to pot arbitrary region to achieve better efficiencies by using PBIs excellent thermal, photochemical, and photophysical features including strong light absorption in the visible spectral range [21].

In this paper, two new PBI-fullerene dyads were synthesized, characterized, utilized to produce efficient singlet oxygen and applied in the photooxidation of DHN to produce juglone as metal free triplet photosensitizers in which one or two PBI (light-harvesting antenna) unit and C₆₀ unit (spin converter) are connected via Bingel Cyclopropanation (**7**, **8**). The molecular structures of PBI derivatives and PBI-fullerene dyads are shown in Scheme 1 and identified by using mass, ¹H and ¹³C and spectroscopic techniques. The photophysical properties of parent perylene derivatives (**5,6**) and perylene-fullerene dyads (**7,8**) were investigated by using UV-Vis absorption and 2D and 3D fluorescence emission studies. The singlet oxygen quantum yields were measured via direct method in different solvents (dichloromethane, acetonitrile, dichloromethane: methanol (9:1;v:v), dimethyl sulfoxide and methanol) and indirect method by interacting photoinduced singlet oxygen in the media with 1,3-diphenylisobenzofuran (DPBF) to generate endoperoxide in dichloromethane to calculate singlet oxygen quantum yield. Besides this phenomenon was also used in the synthesis of juglone via photooxidation of 1,5-dihydroxynaphtalene (DHN) and compared the results with methylene blue.

2. Experimental

2.1. Materials

The deuterated solvent (CDCl₃) for NMR spectroscopy, silica gel, dichloromethane, acetonitrile, dmethyl sulfoxide, methanol and toluene were provided from Merck. Following chemicals were obtained from Sigma Aldrich; ammonium acetate, dihexyl ketone, 1-butanol, malonyl dichloride, methyl malonyl chloride. Perylene-3,4,9,10-tetracarboxylic dianhydride, sodium cyanoborohydride, *t*-butanol, *N,N*-dimethylacetamide, carbon tetrabromide and 1,5-dihydroxynaphtalene were purchased from Acros Organics. Fullerene, potassium hydroxide, zinc acetate, imidazole, sodium azide and pyridine were provided from Alfa Aesar. DBU and 6-amino-1-hexanol was purchased from ABCR and T.C.I Chemicals, respectively.

2.2. Equipment

Electronic absorption spectra were recorded with a Shimadzu 2101 UV spectrophotometer in the UV-visible region. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Singlet oxygen phosphorescence around 1270 nm was determined by using Horiba Jobin-Yvon Fluoremeter with Hamamatsu NIR PMT 5509 at $-80\text{ }^{\circ}\text{C}$. The fluorescence lifetimes were obtained using Horiba-Jobin- Yvon- SPEX Fluorolog 3-2iHR instrument with Fluoro Hub-B Single Photon Counting Controller. Signal acquisition was performed using a TCSPC module. 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. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 solutions on a Varian 500 MHz spectrometer. Elemental analyses were obtained using a Thermo Finnigan Flash 1112 Instrument. 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).

2.3. Synthesis

Compounds **1-4** were prepared according to procedure described previously (Scheme 1) [22].

2.3.1. Synthesis of compound **5**

Compound **4** (50 mg, 0.074 mmol) was dissolved in 15 mL of DCM and pyridine (6.64 mg, 0.084 mmol) was added under Ar atmosphere. The mixture cooled on an ice bath and 5 mL DCM solution of monomethyl malonyl chloride (10.11 mg, 0.074 mmol) was added dropwise. The mixture was stirred for 1 h and the reaction was followed by TLC. The reaction mixture was extracted with DCM/ H_2O , and the organic layer was dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator until the solvent was removed. Compound **5** (red solid) was isolated from column chromatography on silica gel (230-400 mesh) with DCM:MeOH (100:0.5) as the eluent (yield: 64.7%) (mp: $120\text{ }^{\circ}\text{C}$)

Characterization data of **5**: Elemental analyses: Calc. (%) for $C_{47}H_{52}N_2O_8$: C, 73.04; H, 6.78; N, 3.62; found C, 73.0; H, 5.82; N, 4.32. FT-IR (ATR, cm^{-1}) 2954-2952 (C-H str), 1751 (C-H, bending), 1724 (C-H, bending), 1694 (C=O, str), 1645 (C=O, str), 1597 (C=C, str), 1337 (C-N, str), 1246 (C-N, str), 806 (C-H, bending). 1H -NMR (500 MHz, $CDCl_3$, 298 K, δ ppm): 8.61 (m, 2H), 8.53 (d, $J=7.9$ Hz, 2H), 8.48 (d, $J=8.0$ Hz, 2H), 8.43 (d, $J=8.0$ Hz, 2H), 5.23-5.17 (m, 1H), 4.18 (d, $J=6.2$ Hz, 2H), 3.77 (s, 2H), 3.41 (s, 2H), 2.31-2.26 (m, 2H), 1.93-1.89 (m, 2H), 1.78 (s, 2H), 1.74-1.67 (m, 2H), 1.49 (s, 4H), 1.34 (s, 8H), 1.26 (s, 9H), 0.85 (t, $J=6.6$ Hz, 6H). ^{13}C -NMR (126 MHz, $CDCl_3$, 298 K, δ ppm): 167.01, 166.55, 163.14, 134.42, 131.15, 129.40, 129.14, 126.19, 126.11, 122.99, 122.92, 122.80, 65.57, 54.84, 52.48, 41.38, 40.40, 32.38, 31.77, 29.24, 28.33, 27.93, 26.97, 26.68, 25.54, 22.60, 14.05, 1.02. MS (MALDI-TOF) (DIT) m/z (%): Calc.: 772.94; found: 772.33537 $[M]^+$.

2.3.2. Synthesis of compound **6**

Compound **4** (100 mg, 0.148 mmol) was dissolved in 15 mL of DCM and pyridine (14 mg, 0.17 mmol) was added under Ar atmosphere. The mixture cooled on an ice bath and 5 mL DCM solution of malonyl dichloride (10.43 mg, 0.074 mmol) was added dropwise. The mixture was stirred for 4 h and the reaction was followed by TLC. The reaction mixture was extracted with DCM/ H_2O , and the organic layer was dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator until the solvent was removed. Compound **6** was (red solid) isolated from column chromatography on silica gel (230-400 mesh) with DCM:MeOH (100:1) as the eluent (yield: 33.5%) (mp: 150 °C)

Characterization data of **6**: Elemental analyses: Calc. (%) for $C_{89}H_{96}N_4O_{12}$: C, 75.61; H, 6.84; N, 3.96; found C, 75.58; H, 6.82; N, 3.90. FT-IR (ATR, cm^{-1}) 2956-2952 (C-H str), 1749 (C-H, bending), 1724 (C-H, bending), 1693 (C=O, str), 1656 (C=O, str), 1592 (C=C, str), 1338 (C-N, str), 1250 (C-N, str), 1091 (C-O, str), 1010 (C-O, str), 805 (C-H, bending). 1H -NMR (500 MHz, $CDCl_3$, 298 K, δ ppm) 8.45 (m, 4H), 8.38 (d, $J=7.9$ Hz, 4H), 8.26 (d, $J=7.9$ Hz, 4H), 8.21 (d, $J=7.9$ Hz, 4H), 5.19-5.13 (m, 2H), 4.20 (t, $J=6.3$ Hz, 4H), 4.14 (t, $J=7.2$ Hz, 4H), 3.41 (s, 2H), 2.30- 2.22 (m, 4H), 1.94 (d, $J=12.5$ Hz, 4H), 1.84-1.78 (m, 4H), 1.77-1.72 (m, 4H), 1.56-1.51 (m, 8H), 1.38 (s, 13H), 1.28 (s, 21H), 0.87 (t, $J=6.6$ Hz, 12H). ^{13}C -NMR (126 MHz, $CDCl_3$, 298 K, δ ppm): 166.64, 162.93, 133.99, 133.63, 130.81, 129.18, 128.86, 125.77, 125.75, 122.84, 122.65,

122.52, 65.55, 54.91, 41.90, 40.47, 32.37, 31.81, 29.27, 28.38, 27.85, 27.07, 26.75, 25.62, 22.63, 14.07, 1.02. MS (MALDI-TOF) (DIT) m/z (%): Calc.:1413.76; found: 1412.43088 [M-H]⁺.

2.3.3. Synthesis of compound 7

Compound **5** (37 mg, 0.048 mmol) was dissolved in 15 mL of toluene. C₆₀ (57 mg, 0.07 mmol) and CBr₄ (16 mg, 0.048 mmol) was added to the solution. The mixture stirred for 30 min. 10 mL toluene solution of 1,8 diazabicyclo [5.4.0]undec-7-ene (DBU, 15 mg, 0.096 mmol) was added dropwise. The mixture was stirred over night at room temperature. The crude product was subjected to the column chromatography instantly and compound **7** (red solid) was isolated from column chromatography on silica gel (230-400 mesh) with DCM:MeOH (100:0.5) as the eluent (yield: 14%) (mp: 220 °C)

Characterization data of **7**: Elemental analyses: Calc. (%) for C₁₀₇H₅₀N₂O₈: C, 86.16; H, 3.38; N, 1.88; found C, 86.14; H, 6.35; N, 1.83. FT-IR (ATR, cm⁻¹) 2961-2847 (C-H str), 1656 (C=O, str), 1594 (C=O, str), 1261 (C-N, str), 1089 (C-O, str), 1018 (C-O, str), 793 (C-H, bending). ¹H-NMR (500 MHz, CDCl₃, 298 K, δ ppm): 8.67 (m, 2H), 8.65 (d, *J*= 7.5 Hz, 2H), 8.61 (d, *J*= 7.5 Hz, 2H), 8.59 (d, *J*= 7.9 Hz, 2H), 5.21-5.15 (m, 1H), 4.52 (t, *J*= 6.3 Hz, 2H), 4.25 -4.19 (m, 2H), 4.09 (s, 3H), 2.35 (m, 2H), 2.30-2.19 (m, 4H), 1.88 (m, 6H), 1.79 (m, 4H), 1.62 (m, 4H), 1.33 (m, 8H), 0.83 (t, *J*=7.0 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃, 298 K, δ ppm): δ 163.36, 145.12, 144.46, 143.81, 143.67, 142.90, 142.11, 141.78, 140.85, 139.09, 138.74, 134.77, 134.34, 131.47, 129.53, 126.52, 123.15, 123.01, 54.83, 54.03, 40.40, 32.39, 31.93, 31.77, 29.70, 29.24, 28.44, 28.06, 26.95, 26.60, 25.79, 24.77, 22.69, 22.61, 14.12, 14.0. MS (MALDI-TOF) (DHB) m/z (%): Calc.: 1491.58; found: 1493.888 [M+2H]⁺.

2.3.4. Synthesis of compound 8

Compound **6** (35 mg, 0.025 mmol) was dissolved in 15 mL of toluene. C₆₀ (27 mg, 0.037 mmol) and CBr₄ (8.19 mg, 0.025 mmol) were added to the solution. The mixture stirred for 30 min. 10 mL toluene solution of DBU (7.52 mg, 0.05 mmol) was added dropwise. The mixture was stirred over night at room temperature. The crude product was subjected to the column chromatography instantly and compound **8** (red solid) was isolated from column chromatography on silica gel (230-400 mesh) with DCM:MeOH (100:1) as the eluent (yield: 22.8%) (mp: 173 °C)

Characterization data of **8**: Elemental analyses: Calc. (%) for C₁₄₉H₉₄N₄O₁₂: C, 83.93; H, 4.44; N, 2.63; found C, 86.14; H, 6.35; N, 1.83. FT-IR (ATR, cm⁻¹) 2954-2851 (C-H str), 1741 (C-H, bending), 1696 (C=O, str), 1655 (C=O, str), 1592 (C=C, str), 1337 (C-N, str), 1252 (C-N, str), 1087 (C-O, str), 1016 (C-O, str), 809 (C-H, bending). ¹H NMR (500 MHz, CDCl₃, 298 K, δ ppm): 8.46 (m, 2H), 8.41 (d, *J*=7.8 Hz, 2H), 8.27 (d, *J*=7.0 Hz, 2H), 8.23 (d, *J*=8.0 Hz, 2H), 5.19-5.13 (m, 1H), 4.56 (t, *J*=5.2 Hz, 2H), 4.19 (t, *J*=6.5 Hz, 2H), 2.27 (s, 2H), 1.95 (s, 4H), 1.87 (t, *J*=6.0 Hz, 2H), 1.70-1.59 (m, 8H), 1.39 (s, 8H), 0.87 (s, 8H). ¹³C NMR (126 MHz, CDCl₃, 298 K, δ ppm): 163.59, 162.99, 145.26, 145.09, 145.06, 145.02, 144.52, 144.44, 143.71, 142.90, 142.84, 142.81, 142.04, 141.78, 140.80, 138.93, 134.08, 133.65, 130.90, 129.19, 128.94, 125.85, 125.79, 122.86, 122.71, 122.56, 67.38, 54.91, 40.47, 32.38, 31.82, 29.70, 29.28, 28.47, 27.93, 27.08, 26.73, 25.82, 22.64, 14.08, 1.02. MS (MALDI-TOF) (DIT) (m/z) (%): Calc.: 2132.4; found: 2131.31109 [M-H]⁺.

2.4. Photooxidation

The photooxidation experiments were carried out as follows [23, 24]. A DCM:MeOH (9:1; v:v) solution of DHN (2.0x10⁻⁴ M) and a triplet photosensitizer (**7**, **8** and MB) (5 mol% with respect to DHN) was placed in a two-neck round-bottomed flask (10 mL). The solution was then irradiated by using 516 nm and 630 (5 mW/cm²) led lamps. UV/Vis absorption spectra were recorded at intervals of 5 min. The DHN consumption was monitored by following the decrease in the UV absorption at 301 nm, and the juglone production was monitored by increasing at 427 nm. The yield of juglone was calculated from its molar extinction coefficient ($\epsilon=3811\text{ m}^{-1}\text{ cm}^{-1}$) by dividing the concentration of juglone to the initial concentration of DHN ($\epsilon=7664\text{ m}^{-1}\text{ cm}^{-1}$) where the initial concentration of DHN was calculated via dividing its molar extinction coefficient to initial absorbance.

2.5. The parameters for fluorescence quantum yields

The fluorescence quantum yields (Φ_F) of compounds **5-8** were determined by the comparative method (Eq. (1)) [25].

$$\Phi_F = \Phi_{F_{Std}} \frac{F_{Std} \cdot n^2}{F_{Std} \cdot A \cdot n_{Std}^2} \quad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the compounds (**5-8**) and the standard, respectively. A and A_{Std} are the respective absorbances of compounds (**5-8**) 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. Fluorescein ($\Phi_F = 0.95/0.1$ M NaOH) was employed as the standard [26].

2.6. The parameters for singlet oxygen

Singlet oxygen formation (Φ_Δ) measurements were carried out by using Horiba Jobin-Yvon Fluoremeter with Hamamatsu NIR PMT 5509. Singlet oxygen phosphorescence at 1270 nm was detected with monochromator model iHR-320 at -80 °C. The intensity of singlet oxygen formation was obtained via according to the equation,

$$\Phi_\Delta = \Phi_\Delta(std) \times \frac{I_\Delta(dyad) A(std)}{I_\Delta(std) A(dyad)} \quad (2)$$

Singlet oxygen quantum yields of compounds **5-8** were calculated using singlet oxygen trap molecule DPBF and methylene blue (MB) as reference ($\Phi_\Delta = 0.52$ in DCM). Singlet oxygen can be monitored using photobleaching and subsequent decrease in absorbance of DPBF. 516 nm (2.1 mW/cm²) and 630 nm (4.0 mW/cm²) led bulb were used as light source. Light sources were exposed from 5 cm cell distance and absorbances were taken intervals for each solution (Eq. (3)).

$$\Phi_\Delta(dyad) = \Phi_\Delta(ref) \left[\frac{k(dyad)}{k(ref)} \right] \left[\frac{F(ref)}{F(dyad)} \right] \left[\frac{PF(ref)}{PF(dyad)} \right] \quad (3)$$

where *dyad* and *ref* designate the “PBI- 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 is absorption at the irradiation wavelength), and PF is light intensity (energy flux, mW/cm²).

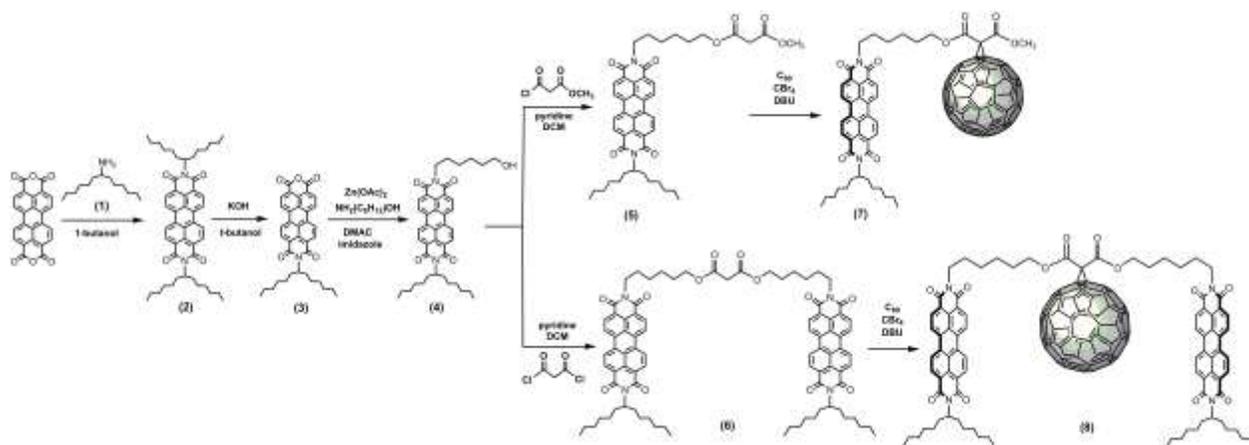
Singlet oxygen quenching experiments were carried out in the presence of sodium azide by using Horiba Jobin-Yvon Fluoremeter with Hamamatsu NIR PMT 5509. Increasing concentration of

sodium azide were added cascade into the solution of compound **7** and **8** and the decrease in the singlet oxygen phosphorescence at 1270 nm were recorded. Later, DPBF and DHN experiments were repeated in the presence of NaN_3 (200 μM) under the same experimental condition.

3. Results and discussion

3.1. Synthesis and Characterization of perylene-fullerene triplet photosensitizers

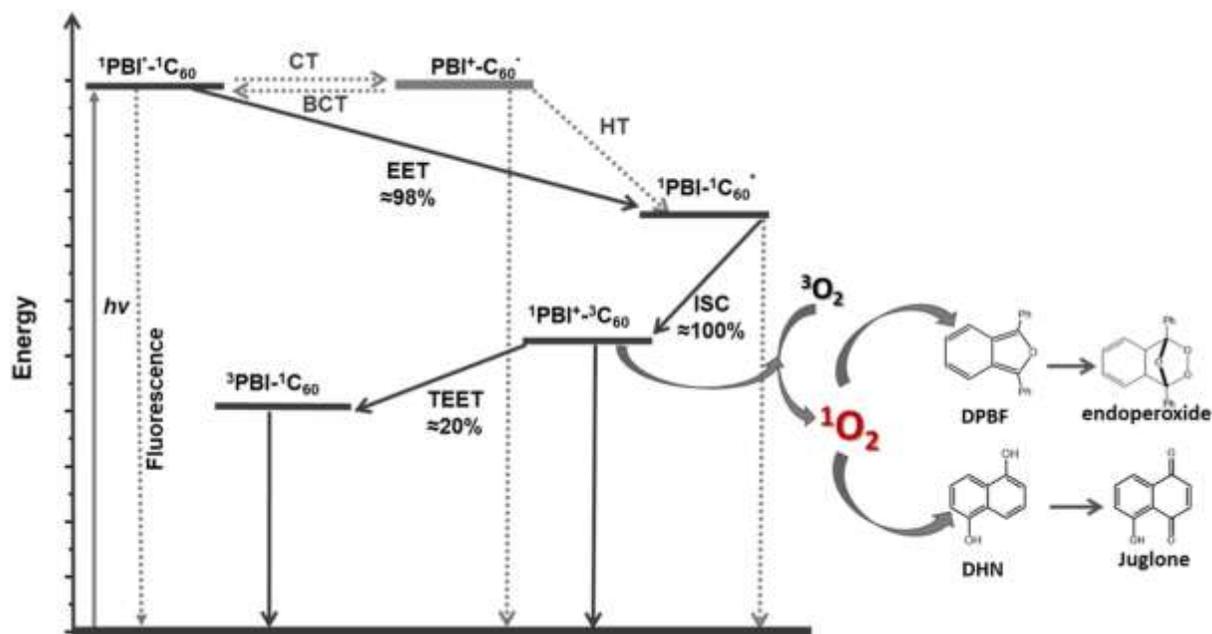
The work on the origin of phosphorescence emission from organic molecules by Kasha and Lewis marked an era and guide the research on triplet excited states [27, 28]. The molecules with efficient triplet excited state capability find usages in photodynamic therapy (PDT), photocatalysis, bio-imaging, sensing and photon up conversion [29-32]. Fullerene- C_{60} is used as omnibus spin convertor, thanks to the intrinsic capability of its ISC [13]. However, the weak absorption of fullerene- C_{60} needs to be considered while designing a fullerene bearing triplet photosensitizer. One approach commonly used in the preparation of triplet photosensitizers is to propose visible light harvesting chromophore to the molecule. As one of the most extensively studied chromophores, PBIs exhibit substantial optical/electronic properties, such as high molar absorptivity, high fluorescence quantum yield and chemical/ photochemical stability [33, 34]. Herein we choose an asymmetric PBI derivatized from “*peri*” positions as light harvester. The syntheses of the PBI-fullerene dyads (**7**, **8**) involved a multistep approach and carried out according to Scheme 1 and the details are given in the Experimental Section. Initially, the asymmetric PBI (**4**) that exhibit absorption ~ 500 nm and host -OH functional group was synthesized by treatment of perylenetetracarboxylic dianhydride with corresponding branched amine (**1**) to obtain symmetric PBI (**2**) following hydrolysis of compound **2** for compound **3**. Compound **3** was then reacted with 6-aminohexanol by using imidazole as basic solvent and zinc acetate to synthesize PBI derivative (**4**). Compound **4** was then reacted with methyl malonyl chloride and malonyl dichloride to generate functional group on PBIs (**5**, **6** respectively) for Bingel Cyclopropanation. Finally, PBIs **5** and **6** were reacted with fullerene- C_{60} to generate PBI-fullerene dyads **7** and **8** respectively. The structural integrity of all compounds (**1-8**) were confirmed by ^1H , ^{13}C NMR and MALDI- TOF- MS and the results were consistent with the assigned formulations (see experimental part and ESI).



Scheme 1. Synthesis of the PBI-Fullerene Dyads

3.2. Photo-physical properties

Triplet photosensitizers (PSs) are molecular systems that should show strong visible light absorption, following an efficient intersystem crossing (ISC) and preferably long-lived triplet excited state [35, 36]. This photoinduced triplet excited energy state's lifetime long enough to be able to transfer to ground state (triplet) molecular oxygen ($^3\text{O}_2$) to generate singlet excited state of oxygen ($^1\text{O}_2$). This photoinduced triplet excited energy state's lifetime long enough to be able to transfer to ground state (triplet) molecular oxygen ($^3\text{O}_2$) to generate singlet excited state of oxygen ($^3\text{O}_2$). Hofmann *et al.* reported detailed explanation of the photophysical processes in PBI- C_{60} systems [20]. An efficient electronic excitation energy transfer (EET) from the PBI ($^1\text{PBI}^*-\text{C}_{60}$) to the fullerene ($^1\text{PBI}-\text{C}_{60}^*$) ensuing affluent ISC ($^1\text{PBI}^+-\text{C}_{60}$) then followed by a back-transfer of the excitation energy (triplet-triplet energy transfer, TEET) from the fullerene to the PBIs triplet state ($^3\text{PBI}-\text{C}_{60}$) (Scheme 2). Unlike previously reported chromophore-fullerene dyad systems, negligible charge-transfer process from the excited state of the PBI to the fullerene occur [13, 37, 38]. Benefiting from the addition of the fullerene as spin converter, the ISC efficiency of dyads **7** and **8** were expected to be enhanced compared with PBI derivatives (**5** and **6**), deployed us to investigate the photophysical behavior of synthesized compounds in solutions.



Scheme 2. Possible photophysical mechanisms of the PBI -fullerene triad. Abbreviations: EET is electronic excitation energy transfer, ISC stands for intersystem crossing, CS is charge separation. HS is hole transfer and TEET is for triplet-triplet energy transfer,[20].

Since fullerene- C_{60} is a spherical π -system, UV/vis absorption spectroscopy is a helpful tool for fullerenes and their derivatives [39]. The UV/vis absorption spectrum of fullerene- C_{60} display allowed absorption below ~ 400 nm with spin forbidden transition at 625 nm [40, 41]. Chemical functionalization from outside of the fullerene cage highly affect the electronic structure and π -system [42]. UV-visible absorption spectra of the pristine fullerene- C_{60} in dichloromethane solution ($2\mu\text{M}$) was recorded. As shown in Fig. 1A, the absorption of fullerene- C_{60} exhibit maxima at 329 nm. UV/Vis absorption studies of compounds **5-8** demonstrated that the absorption profiles of dyads (**7** and **8**) have similar features compared to the absorption spectrum of parent compounds (**5** and **6**) and fullerene- C_{60} except for the intensity differences (Figure 1A). The absorption spectrum of the dyads (**7** and **8**) displayed maxima around 525, 490, 460, 425 and 325 nm. All four compounds (**5-8**) showed high molar extinction coefficients ($\epsilon=7.72- 11.12\times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) which maintain the first requirement to be an efficient photosensitizer. It is note that one PBI substituted malonyl derivative **5** was optically different than the fluorescence spectrum of bis-perylene substituted malonyl derivative **6** (Figure 1B). Compound **5** exhibited strong

emissions ~532 and ~573 nm and a weak emission ~624, that is consistent with perylene fluorescence [43] while bis-PBI substituted malonyl derivative **6** fluorescence emission ~623 nm became more severe in same concentration with the compound **5**. On resonant excitation of pyrene or perylene in solution, it is proverbial that excimer luminescence is generally observed for pyrene at high concentration [44-46] whereas it is described to be difficult to notify excimer with perylene derivatives in solution even at saturated concentration [47-49]. Thus, we appointed the perylene excimer on a dilute solution (0.1 μM) of molecule thanks to the π - π interaction between the perylenes but not in the same concentrate solutions of compound **5**. Therefore, it is resulted that red-shifted emission of compound **6** is formed owing to intramolecular excimer emission among the substituted asymmetric peryleneoxy groups. Upon excitation at the perylene units PBI derivatives **5** and **6** showed fluorescent emissions and the fluorescent quantum yields were calculated to be $\Phi_{\text{F}}= 0.51$ and 0.24 respectively. The fluorescent quantum yields were totally diminished with the successive addition of fullerene at the PBIs (**7** and **8**) that secure another state for a good PS.

3D spectra of compounds **5-8** were measured in dichloromethane to evaluate the transitions between absorptions and emissions (Figure 2). 3D- fluorescence spectra of all compounds (**5-8**), were found to be in agreement with 2D- fluorescence emission measurements. The strongest transitions for compound **5** and **6** were occurred at excitation at ~485 and ~522 nm where the strongest emissions appeared at ~535 nm whereas the fluorescence emissions of dyads **7** and **8** at the same area were effectively quenched. Also, the 3D maps of **5-8**, were found to be well correspondence with Kasha's rule [50, 51]. Via using the time-correlated single photon counting (TCSPC) technique, the emission decay profiles of compounds **5-8** were measured in DCM at room temperature. Compounds **5** and **6** featured a monoexponential decay with $\tau= 4.01$ and 3.00 ns respectively and fluorescence lifetimes of dyad systems couldn't be detected with a nano level device since the lifetimes of the dyads (**7, 8**) are probably in picosecond levels (Figure S30).

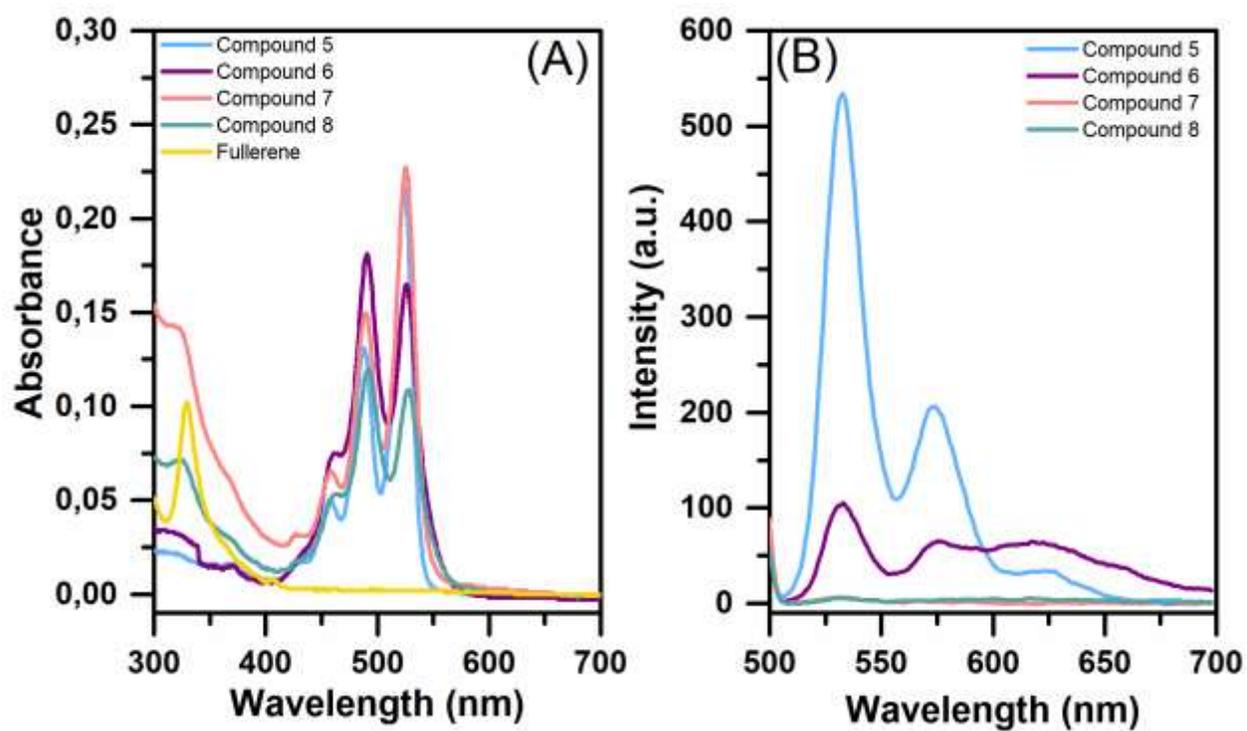


Figure 1 Electronic (A) absorption (2 μM , **5-8**, fullerene) (B) emission (0.1 μM , **5-8**) spectra in dichloromethane.

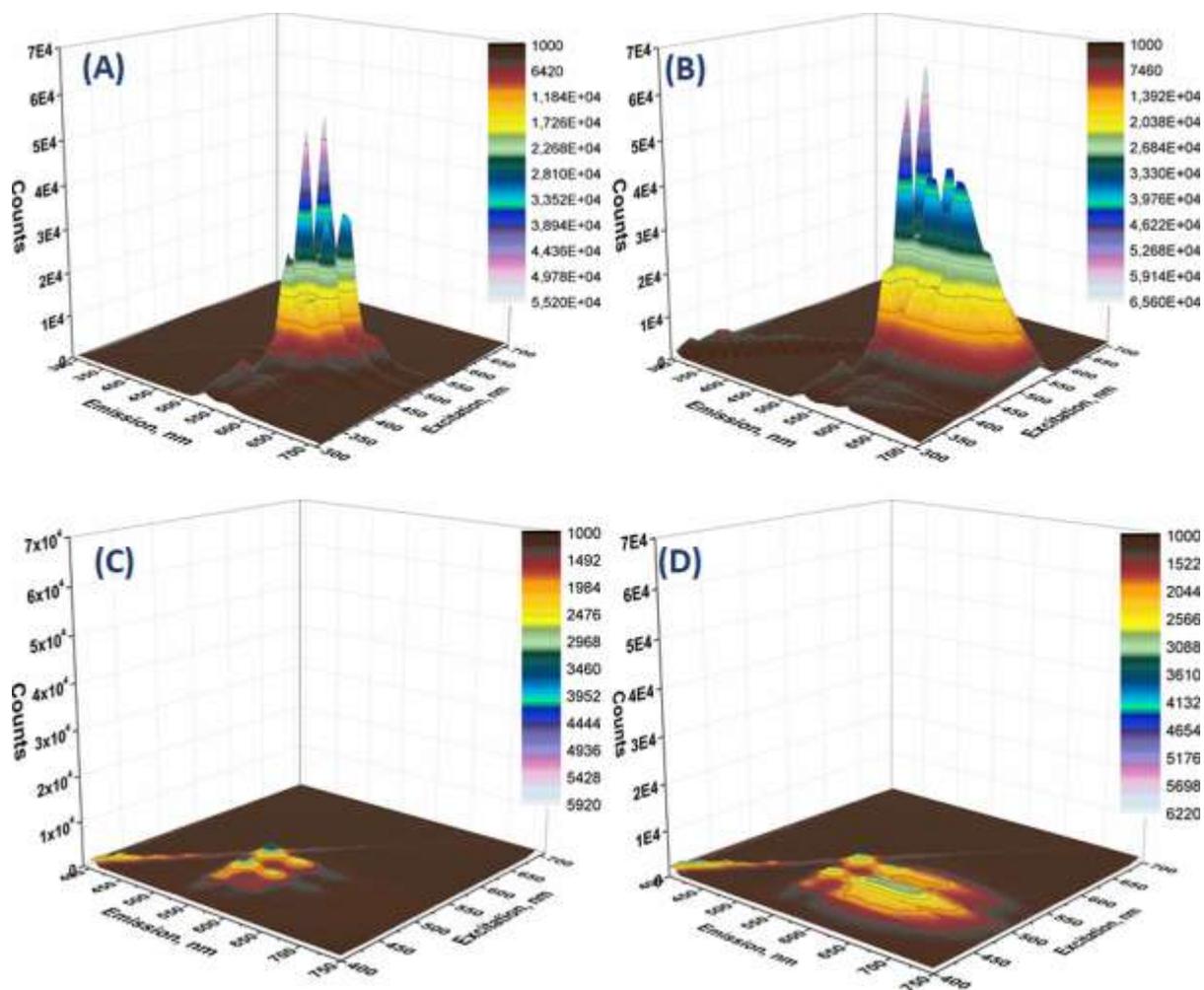


Figure 2 3D fluorescence emission maps of compounds (A) 5, (B) 6, (C) 7 and (D) 8 in DCM (0.1 μM)

3.3. Photochemical Properties

3.3.1. Singlet oxygen measurements

Although PBIs are known as dyes with high fluorescence quantum yields, the presence of fullerene in the system indisputably accelerate ISC from singlet to triplet-excited state. The formation of $^1\text{O}_2$ demand aerobic conditions [52, 53]. First, singlet-oxygen phosphorescence for dyads (**7** and **8**) at 1270 nm were aimed to detect in different solvents. Dyads (**7** and **8**) excited at their absorption maxima with a xenon-arc source and detected with near-IR sensitive detector. The equal concentrations (2 μM) of dyads (**7** and **8**) for all solvents were carried out and dichloromethane following the dichloromethane: methanol (9:1; v:v) solutions for both dyads gave the strongest singlet oxygen phosphorescence emissions at its brand wavelength (nm) around 1270 nm (Figure 3A and 3B). To correlate the singlet oxygen generation of both dyads for each solvent, the area under the phosphorescence emission divided to the absorbance of the dyad in the related solvent (Figure S31). Figure 3C exhibit the bar graphic of the ratio of phosphorescence area (I) to the absorbance of the dyad (A) which propound the singlet oxygen generation happen more powerfully in dichloromethane and dichloromethane: methanol (9:1; v:v).

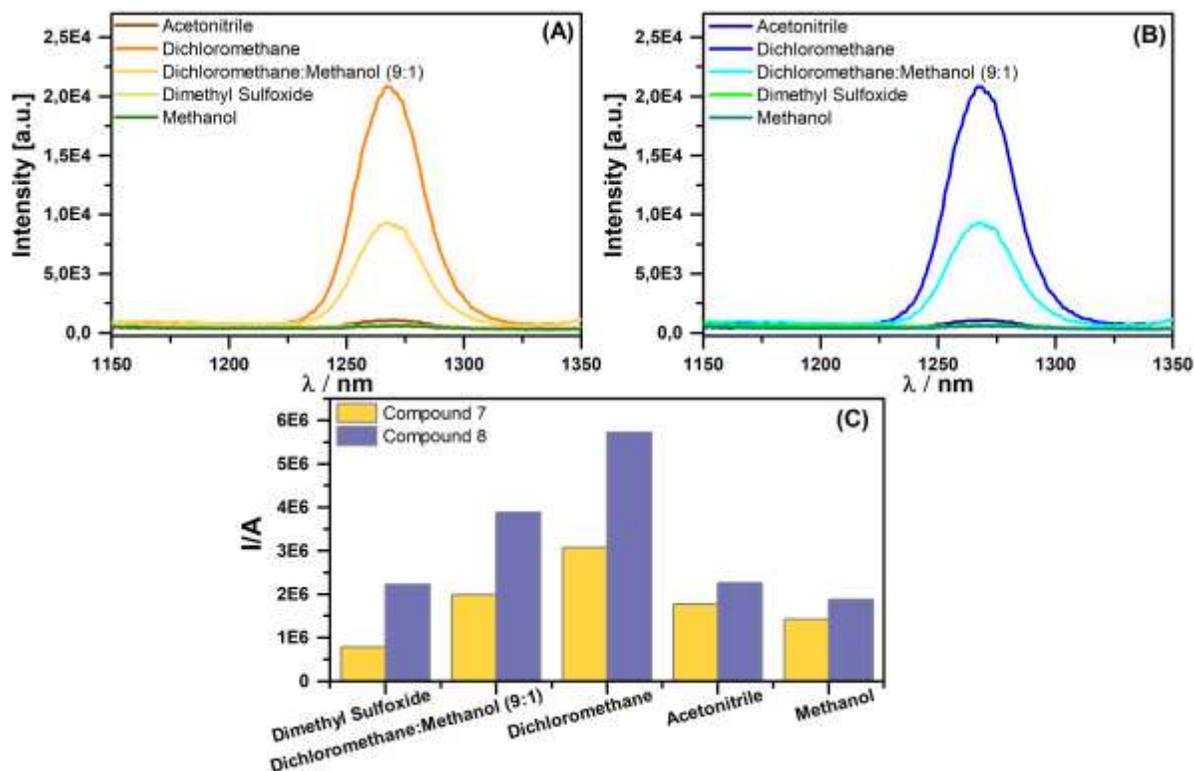


Figure 3. Singlet oxygen phosphorescence with sensitization in different solvents from (A) compound 7, (B) compound 8 and (C) the ratios of emission intensities (I) to absorbance (A) for compound 7 and 8

Then we went for quantitative assessment of singlet oxygen generation experiments via indirect method, the solvents first bubbled with oxygen for 5-10 min. The singlet oxygen generation and the quantum yield of singlet oxygen production via formation of endoperoxide from DPBF to produce 1,2-dibenzoylbenzene by PBI-fullerene dyads (**7** and **8**) were measured in dichloromethane since via direct method dichloromethane induced highest production of singlet oxygen. Methylene blue was used as the reference photosensitizer. Upon irradiation at the PBI units by using green led light (516 nm, 2.1 mW/cm²), PBI-fullerene dyads (**7** and **8**) do generate singlet oxygen with splendid efficiencies; the quantum yields of singlet oxygen generation were found to be 0.93 and 0.95 respectively which is very much close to ideal quantum yield of singlet oxygen ($\Phi_{\Delta(\max)} = 1.0$) (Figure 4., Table 1). On the other hand, the PBI derivatives (**5** and **6**) were also did not show any singlet oxygen production (Figure S33 and S34). The photostability is also substantial for photosensitizers. Thus, the photostability's of the dyads (**7** and **8**) and were investigated for 30 min in dichloromethane solutions (Figure S36, ESI). Upon excitation via

green led light absorbances of dyads showed no significant changes. The singlet oxygen production abilities in these systems are mainly depending on the production of a long-lived triplet state [54-56], the excellent quantum yield values of $^1\text{O}_2$ and the high extinction coefficients of the PBI moieties in the visible range, make these dyad systems ideal triplet photosensitizers to be used in organic photooxidation reactions or other singlet oxygen-base processes that use light as an energy source. Since the efficiency of these molecules are found to be excellent, the reactive oxygen species resulting from these processes can also be used in the photooxidation reactions processes such as synthesis of juglone starting from DHN.

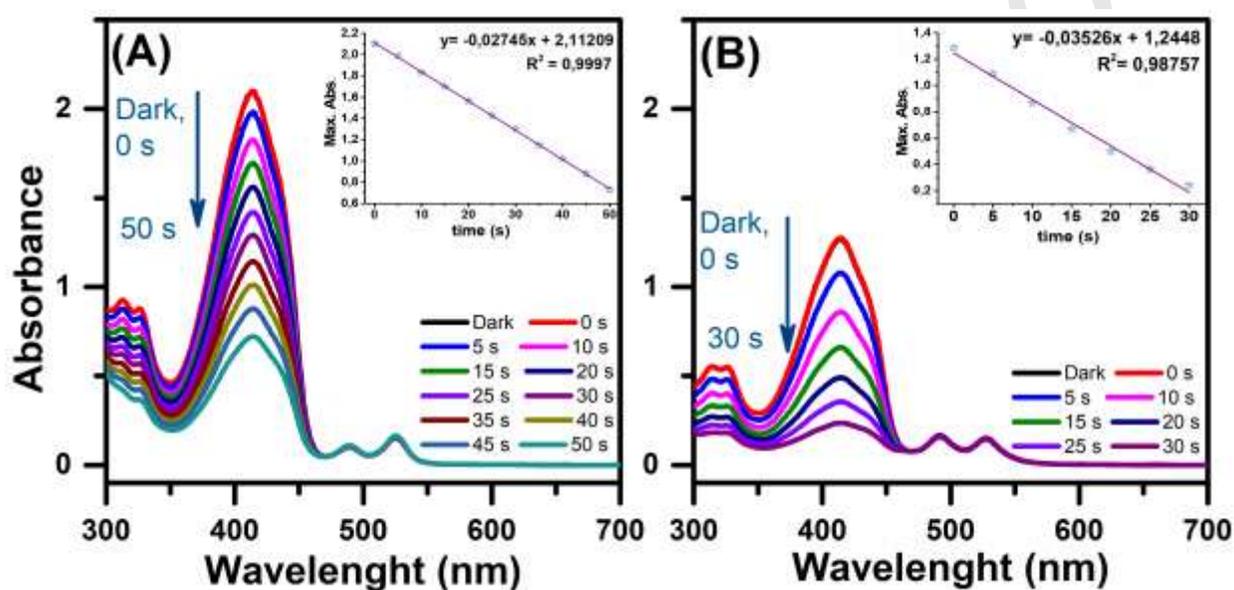


Figure 4 Decrease in absorbance spectrum of DPBF in the presence of (A) compound **7** ($2\ \mu\text{M}$), (B) compound **8** ($2\ \mu\text{M}$) in dichloromethane.

3.3.2. Photooxidation measurements

The photooxidation reactions were studied in order to apply the synthesized dyad systems in the synthesis of juglone starting from DHN with green light irradiation in organic solvent as we are interested in observing the applicability of the dyads and the efficiencies via comparison with the conventional photosensitizers. Photooxidation with the PBI-fullerene dyads (**7** and **8**) and as conventional triplet photosensitizer MB were studied. The triplet photosensitizers (**7**, **8**, **MB**) were photoexcited upon light absorbing units, $^1\text{O}_2$ was generated. Since the half-life of $^1\text{O}_2$ was

long enough to react with DHN, it photooxidized DHN in the reaction media to produce juglone. The juglone generations were monitored by the UV/Vis absorption increment of juglone at 427 nm and reduction of DHN absorption (301 nm) (Figure 5) [16, 23, 24, 57, 58]. In order to facilitate correlation with the proficiency of the synthesized heavy atom free triplet photosensitizers (**7** and **8**) and MB maximum absorbance of juglone or DHN against the irradiation time were plotted (Figure 6). As expected, the efficiencies of the dyads are much better and drastic than MB according to the slopes of the lines, where the performance of the dyads were similar with each other. The yield of juglone after 30 min. calculated as 95% for both PBI-fullerene dyads (**7** and **8**).

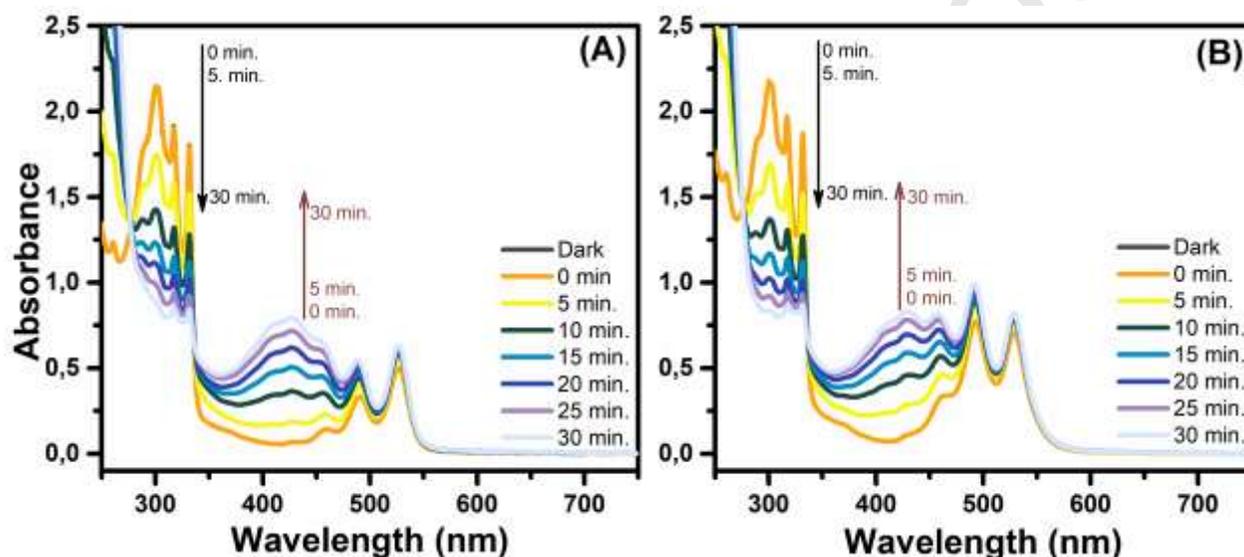


Figure 5 UV/Vis absorption changes upon the photooxidation of DHN with A) dyad **7** and B) dyad **8** as heavy atom free triplet photosensitizers.

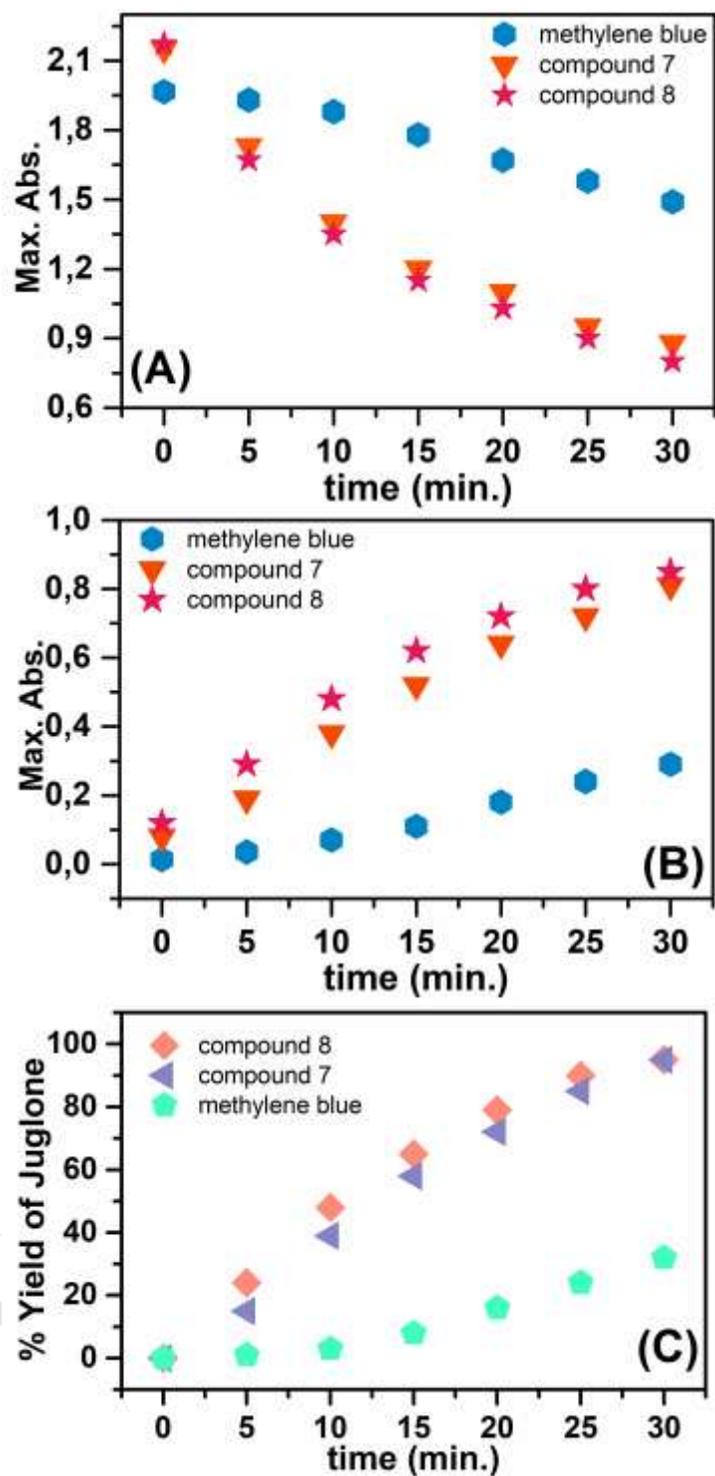


Figure 6 Photooxidation of DHN with perylene-fullerene dyads (**7** and **8**) and MB, Plots of **A**) Maximum absorbance vs. irradiation time (min.) for the photooxidation of DHN, **B**) Maximum absorbance vs. irradiation time (min.) for the production of juglone, **C**) % Juglone yield vs. irradiation time (min.) for the production of juglone,

Sodium azide (NaN_3) is a known and generally employed specific singlet oxygen quencher, especially in the determination of $^1\text{O}_2$ involvement in oxidation processes [59]. The quenching effect of NaN_3 on singlet oxygen was studied both in the $^1\text{O}_2$ phosphorescence and photooxidation (with DPBF and DHN) measurements. First to determine the required NaN_3 concentration to diminish the production of the singlet oxygen, singlet oxygen phosphorescence for dyads (**7** and **8**) at 1270 nm were measured in the presence of various concentration of NaN_3 . Figure S37 shows how the addition of NaN_3 to the solution is able to quench the intensity the phosphorescence peak at 1270 nm. Complete quenching of the singlet oxygen signal with addition NaN_3 left a remaining emission which can be ascribed to the low solubility of NaN_3 in studied solvent (dichloromethane). The azide concentrations after a certain concentration (140 μM) did not notably influenced the singlet oxygen phosphorescence. Then the photooxidation measurements with DPBF and DHN were repeated in the presence of proper amount of NaN_3 (Figure. S38 and S39) which revealed a strong influence of the azide anion on the $^1\text{O}_2$ production process whereas upon irradiation the absorbance intensities of the DPBF (414 nm) and DHN (301 nm) diminished much less than the measurements without a singlet oxygen scavenger. For compounds **7** and **8** the decomposition ratios of DPBF via addition of NaN_3 were decreased from 65% (in 50 s) and 86% (in 30 s) to 27% and 22%. These results affirmed the quenching efficiency increases with solvent polarity [59].

Conclusion

We have successfully prepared and characterized new PBI-fullerene dyads in which a fullerene stands one or two PBI moiety. After cycloaddition of the PBI moieties to the fullerene, triplet excited state was populated, and fluorescence emission was quenched thanks to the fullerene who act as spin converter. The singlet oxygen quantum yields of dyads (**7** and **8**) were determined to be 0.93 and 0.95 which is perfect and number of PBI unit does not affect the singlet oxygen generation distinctly as expected indicating certified that the lack of relationship between molecular structure and singlet oxygen production. In addition, the photoinduced generation of singlet oxygen used in the photooxidation reaction of DHN to synthesize juglone and was consistent with the singlet oxygen quantum yields that the new heavy atom free triplet photosensitizers (**7** and **8**) stronger than the conventional photosensitizer MB and can be used as reaction center in different photocatalysis reactions.

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Table 1. Photophysical and Photochemical features of compounds **5-8**

Compound	Absorption	Emission	^a ϵ , 10 ⁴ (M ⁻¹ cm ⁻¹)	^b Φ_F	^c τ_F (ns)	^d Φ_Δ	^e Yield of juglone (%)
	Wavelength λ_{ab} (nm)	Wavelength λ_{em} (nm)					
5	524, 487, 457, 426	624, 573, 532	8.82	0.51	4.01	0.07	-
6	525, 490, 459	623, 575, 533	11.12	0.24	3.00	0.13	-
7	525, 489, 458, 425, 325	-	7.72	†-	‡-	0.93	95
8	527, 491, 462, 425, 325	-	6.56	†-	‡-	0.95	95

^aMolar extinction coefficients ^aMolar extinction coefficients [calc. for 524 nm (compounds **5** and **7**) and 490 nm (compounds **6** and **8**)], ^bFluorescence quantum yield, ^cFluorescence lifetime ^dSinglet oxygen quantum yield, ^eAfter photoirradiation of 30 min. † below 1% ‡ below nanosecond level