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Introduction

With wide application in various fields, including photovoltaics,^{1,2} photocatalytic organic reactions,^{3–5} photodynamic therapy,⁶ and triplet–triplet annihilation (TTA) upconversion,^{7–9} triplet photosensitizers have attracted extensive attention in recent years. Conventional triplet photosensitizers, such as porphyrins,^{10–12} chromophores with heavy atoms,¹³ or transition metal complexes,^{3,14} suffer from several drawbacks, *e.g.* environmental unfriendliness, high cost and unpredictable intersystem crossing after derivatization.^{4,15,16} In consequence, chemists are devoted to devising novel triplet photosensitizers with unique molecular structures.

Benefiting from the high intrinsic intersystem crossing (ISC) efficiency of fullerenes,^{17,18} metal-free or heavy-atom-free organic systems with fullerenes as acceptors are preferable candidates



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The effect of bridge length on singlet oxygen generation has been studied by designing two rigid axially symmetrical C_{60} -BODIPY triplet photosensitizers: C_{60} -B1 and C_{60} -B2, with different bridge lengths. Rigid phenyl and diphenylacetylene are selected as linkers in C_{60} -B1 and C_{60} -B2, respectively, and the bridge length of C_{60} -B2 is about 6.9 Å longer than that of C_{60} -B1. The photochemical and photophysical properties of the dyads are investigated using steady-state and transient spectroscopies, as well as theoretical calculations. Higher efficiency of energy transfer and higher yield of the triplet C_{60} in C_{60} -B1 are detected. To investigate the effect of bridge length on singlet oxygen generation, the photooxidation reactions of 1,5-dihydroxynaphthalene (DHN) have been carried out with C_{60} -B1, C_{60} -B2, and the reference compounds as photosensitizers. Higher quantum yield of singlet oxygen is generated in C_{60} -B1 (0.82) with a shorter bridge compared to that in C_{60} -B2 (0.59). The photooxidation rate constant of C_{60} -B1 is 1.4 times as that of C_{60} -B2 and 1.3 times as that of MB. The results obtained here are helpful for designing novel donor-bridge-acceptor triplet photosensitizers.

for novel triplet photosensitizer motifs.^{16,18-21} Owing to the weak absorption of fullerene in the visible range,^{17,22,23} organic chromophores, such as boron dipyrromethene (BODIPY),²⁴⁻²⁸ rhodamine²⁹ or perylene³⁰ derivatives, which possess good solubility, high photostability, intense electronic absorption and strong fluorescence bands in the visible and nearinfrared (NIR) region, are selected as the donor units. To design these D-A (donor-acceptor)-based triplet photosensitizers, many complex photophysical processes including singlet energy transfer or electron transfer,^{18,24,31} triplet energy transfer or electron transfer,^{21,24,32,33} and even backward energy transfer or electron transfer^{19,30,34} should be taken into considerations, because these photophysical processes are crucial factors for the photosensitizing abilities of these compounds. Besides the first reduction potentials, the bridge linking donor and acceptor is also a crucial factor for these photophysical processes.^{35–37} To date, several kinds of bridges have been reported to connect acceptor units with organic chromophores.4,6,18,35,38-40 Among these systems, the influence of bridge length on the rate of energy transfer has been studied.4,35 However, the relationship between bridge length and singlet oxygen generation of these triplet photosensitizers is still unclear. To understand the effect of bridge length on singlet oxygen generation is of great importance for designing novel triplet photosensitizers.

In this study, we demonstrated the influence of bridge length on the singlet oxygen generation by designing two rigid

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[†] Electronic supplementary information (ESI) available: Nanosecond timeresolved transient absorption spectroscopy of **R1** and **R2**, the spectral response of DHN and DHN with **R1**, **R2** and MB as the sensitizers, the photostability of C_{60} -**B1** and C_{60} -**B2**, calculation details, high resolution mass spectra, as well as the NMR spectra of the synthesized compounds. See DOI: 10.1039/d0nj05085g



Fig. 1 The structures of $C_{60}\mbox{-}B1, C_{60}\mbox{-}B2, R1$ and R2. The bridge lengths of $C_{60}\mbox{-}B1$ and $C_{60}\mbox{-}B2.$

axially symmetrical C₆₀-BODIPY systems: C₆₀-B1 and C₆₀-B2, with different bridge lengths (Fig. 1). To exclude the influence of spatial interactions because of the different folded conformers,^{34,35,37,41,42} rigid phenyl and diphenylacetylene are selected as linkers in C₆₀-B1 and C₆₀-B2, respectively. To further simplify the photophysical processes of the two dyads, the *meso* position of BODIPY was connected to the nitrogen atom of the fulleropyrrolidine to form axially symmetrical systems. According to the data of molecular structure optimization at the CAM-B3LYP/3-21G level, the bridge length of C₆₀-B2 is about 6.9 Å longer than that of C₆₀-B1.

Experimental section

General

Materials. CDCl₃ was purchased from Sigma-Aldrich. Silica gel, dichloromethane (DCM), ethyl acetate (EAC), petroleum ether (PE), carbon disulfide, tetrahydrofuran (THF), ethanol (EtOH), potassium carbonate, potassium hydroxide (KOH), methanol, anhydrous sodium sulphate (Na₂SO₄), trifluoroacetic acid, 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ), triethylamine, boron trifluoride diethyl etherate, *p*-nitrobenzaldehyde and hydrazine hydrate were obtained from Sinopharm Chemical Reagent Co., Ltd. C₆₀, 2,4-dimethylpyrrole, 4-(2-(trimethylsilyl) ethynyl)benzaldehyde, ethyl bromoacetate, Pd/C, trimethylsilyl lacetylene, Pd₂(dba)₃, *p*-iodoaniline, PPh₃ and ethyl glyoxalate were purchased from Alfa Aesar. THF was distilled over sodium and benzophenone, and all other chemicals used for the synthesis were used directly.

Apparatus. ¹H, ¹³C and ¹⁹F NMR spectroscopies were carried out on BRUKER 300 and 400 MHz spectrometers. HRMS analyses were performed using a Bruker ultrafleXtreme MALDI TOF/TOF. The room-temperature UV-vis absorption and fluorescence spectra were recorded using an absorption spectrometer (UV-1800, Mapada) and a fluorescence spectrophotometer (FP8500, JASCO), respectively. The fluorescence lifetime measurements of **R1**, **C**₆₀-**B1** and **C**₆₀-**B2** were performed at room temperature *via* a time-correlated single photon counting (TCSPC) apparatus with a pulsed laser at a wavelength of 475 nm as the excitation source. A nanosecond flash photolysis system with a pulse laser (7 ns, 10 Hz) from a Nd:YAG at a wavelength of 532 nm as the pump source was used to record the nanosecond transient absorption spectra. All samples were dissolved in 10 mm path length quartz cells and deoxygenated by bubbling nitrogen for over 20 min before measurement. Least-squares regression using a custom-written algorithm in the Matlab was used to fit the decay curves. Quantum calculations were performed using the Gaussian 09 package. The molecular structure optimization and excited-state property calculations were performed at the CAM-B3LYP/3-21G level.

Photooxidation details. A mixture of DHN in a concentration of 1.0×10^{-4} mol L⁻¹ and triplet photosensitizer in a concentration of 1.0×10^{-5} mol L⁻¹ was dissolved in DCM/MeOH (9:1, v/v) in a 25 mL one-neck flask equipped with a gas inlet adaptor, and O₂ was bubbled through the solution for 10 min. The solution was then placed in a quartz cell and irradiated with a 150 W xenon lamp through a narrow band cutoff filter (DT500, 500 nm). The spectral responses of DHN were recorded at intervals of 5 min at 301 nm using a UV-vis spectrophotometer.¹⁸

Photostability details. The photostability of C_{60} -B1 and C_{60} -B2 was studied under similar conditions as the photooxidation experiment without DHN. C_{60} -B1 and C_{60} -B2 at a concentration of 1.0×10^{-5} mol L⁻¹ were dissolved in DCM/MeOH (9:1, v/v). The solution was placed in a quartz cell and irradiated with a 75 W xenon lamp continuously for 1 hour. The spectral responses of C_{60} -B1 and C_{60} -B2 were recorded using a UV-vis spectrophotometer at 0 hour and 1 hour, respectively.

Synthesis

R2 was prepared as per ref. 43.

Synthesis of BODIPY 1. 4-Nitrobenzaldehyde (0.4530 g, 3.0 mmol) and 2,4-dimethylpyrrole (0.7221 g, 7.6 mmol) were dissolved in freshly distilled THF (90 mL) in an oven-dried, 250 mL 3-neck flask equipped with a gas inlet adaptor under an atmosphere of nitrogen. The mixture was stirred at room temperature for 30 min. Then trifluoroacetic acid (2 drops) was added and the mixture was stirred in a N2 atmosphere at room temperature for 12 h. DDQ (0.7080 g, 3.1 mmol) was dissolved in 10 mL of THF and then was added dropwise to the mixture within 25 min. After being stirred for 4 h at room temperature, triethylamine (18 mL) was added to the mixture dropwise within 30 min under ice bath conditions. After being stirred for 5 min, boron trifluoride etherate (18 mL) was added to the mixture dropwise within 30 min. The mixture was stirred at room temperature for 12 h and monitored by TLC. Then 100 mL of water was added to the reaction mixture to quench the reaction. The mixture was transferred to a 500 mL separatory funnel, extracted with DCM (100 mL) and the phases were separated. The aqueous layer was extracted with DCM (2×50 mL). The combined organic layer was washed with saturated brine (200 mL), dried with anhydrous Na₂SO₄, filtered and concentrated. The residue was purified on a silica gel column using DCM/PE (1:2) as the eluent to give 1^{44} as an orange solid (642.0 mg, 58%). ¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, I = 8.8 Hz, 2H, phenyl ring *H*), 7.54 (d, J = 8.8 Hz, 2H, phenyl ring *H*), 6.02 (s, 2H, pyrrole ring H), 2.57 (s, 6H, CH₃), 1.36 (s, 6H, CH₃).

Synthesis of BODIPY R1. Compound 1 (370.0 mg, 1.0 mmol) was dissolved in EtOH (50 mL) in a 100 mL 3-neck flask equipped with a gas inlet adaptor. The mixture was stirred under an atmosphere of nitrogen at room temperature for 30 min. Then hydrazine hydrate (0.6 mL) and Pd/C (56.16 mg) were added. The solution was refluxed at 100 °C until 1 disappeared (2 h). Then the reaction mixture was filtrated and the solvent removed. The residue was purified by silica gel column chromatography using DCM/PE (1:1) as the eluent to give **R1**⁴⁴ as an orange solid (323.0 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ 7.01 (d, J = 8.5 Hz, 2H, phenyl ring H), 6.78 (d, J = 8.5 Hz, 2H, phenyl ring H), 5.97 (s, 2H, pyrrole ring H), 3.85 (bs, 2H, NH₂), 2.54 (s, 6H, CH₃), 1.49 (s, 6H, CH₃); UV-vis (toluene) λ_{max} /nm 370 (4214 L mol⁻¹ cm⁻¹), 475 (15 404 L mol⁻¹ cm⁻¹), 502 (73 903 L mol⁻¹ cm⁻¹).

Synthesis of BODIPY 2. Compound R1 (0.1772 g, 0.52 mmol) and potassium carbonate (0.1088 g, 0.79 mmol) were dissolved in DMF (1.5 mL) in an oven-dried, 25 mL one-neck flask equipped with a gas inlet adaptor under an atmosphere of N₂. After being stirred at room temperature for 30 min, ethyl bromoacetate (70 µL, 0.63 mmol) was added using a syringe. Then the mixture was stirred at 60 $^\circ C$ until the reaction was judged to be complete by TLC (9 h). The solvent was removed in vacuo and the mixture was isolated by silica gel column chromatography using PE/EAC (5:1) as the eluent to afford 2 as an orange solid (0.1823 g, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.04 (d, J = 8.3 Hz, 2H, phenyl ring H), 6.69 (d, J = 8.3 Hz, 2H, phenyl ring H), 5.96 (s, 2H, pyrrole ring H), 4.89 (bs, 1H, NH), 4.27 (q, J = 7.1 Hz, 2H, OCH₂CH₃), 3.95 (s, 2H, NHCH₂), 2.54 (s, 6H, pyrrole ring CH₃), 1.47 (s, 6H, pyrrole ring CH₃), 1.31 $(t, J = 7.1 \text{ Hz}, 3H, \text{ OCH}_2CH_3);$ ¹³C NMR (100 MHz, CDCl₃) δ 170.85 (C=O), 155.06, 147.61, 143.32, 142.74, 132.19, 129.11, 124.28, 121.05, 113.34, 61.62 (OCH₂CH₃), 45.74 (NHCH₂), 14.77 (pyrrole ring CH_3), 14.68 (pyrrole ring CH_3), 14.33 (OCH_2CH_3); ¹⁹F-NMR (376 MHz, CDCl₃) δ –146.24 (q, J = 33.1 Hz); HRMS (MALDI-TOF) m/z calcd for $C_{23}H_{26}BF_2N_3O_2$ [M⁺] 425.2085, found 425.2077.

Synthesis of C₆₀-B1. BODIPY 2 (85.2 mg, 0.2 mmol) and C₆₀ (72.0 mg, 0.1 mmol) were dissolved in 1,2-dichlorobenzene (6 mL). The mixture was stirred under N₂ at room temperature for 30 min. Then ethyl glyoxalate solution (98 µL, 0.5 mmol) was added, and the mixture was stirred at 170 $^\circ \mathrm{C}$ for 4 h. After the solvent was removed under reduced pressure, the mixture was purified by column chromatography on silica gel with CS₂/DCM (1:1) as the eluent to give C₆₀-B1 as a brown orange powder (36.9 mg, 30%). ¹H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, J = 8.3 Hz, 2H, phenyl ring *H*), 7.37 (d, *J* = 8.4 Hz, 2H, phenyl ring *H*), 6.57 (s, 2H, CHCO₂), 6.02 (s, 2H, pyrrole ring H), 4.33-4.14 (m, 4H, OCH₂CH₃), 2.58 (s, 6H, pyrrole ring CH₃), 1.54 (s, 6H, pyrrole ring CH_3 pyrrole ring CH_3), 1.22 (t, J = 7.1 Hz, 6H, OCH_2CH_3); ¹³C NMR (75 MHz, CDCl₃) δ 169.99 (*C*=O), 155.66, 153.20, 150.17, 147.68, 146.68, 146.64, 146.58, 146.31, 145.96, 145.85, 145.74, 145.72, 145.69, 145.53, 145.47, 144.71, 144.63, 143.30, 143.12, 142.95, 142.87, 142.39, 142.32, 142.12, 142.01, 141.99, 141.85, 141.42, 140.41, 139.85, 136.98, 136.21, 131.89, 129.33, 128.68, 121.42, 119.50, 74.76 (CHCO₂), 71.09 (sp³-C of C₆₀),

62.15 (OCH₂CH₃), 14.77 (pyrrole ring *C*H₃), 14.68 (pyrrole ring *C*H₃), 14.39 (OCH₂CH₃); ¹⁹F-NMR (376 MHz, CDCl₃) δ –146.22 (q, *J* = 31.6 Hz); FT-IR ν /cm⁻¹ (KBr) 2962, 1709, 1675, 1589, 1545, 1506, 1406, 1340, 1317, 1284, 1198, 1085, 982, 879, 834, 751, 580, 526; HRMS (MALDI-TOF) *m*/*z* calcd for C₈₇H₃₀BF₂N₃O₄ [M^{•-}] 1229.2316, found 1229.2302; UV-vis (toluene) λ_{max} /nm 313 (39487 L mol⁻¹ cm⁻¹), 431 (5716 L mol⁻¹ cm⁻¹), 476 (19178 L mol⁻¹ cm⁻¹), 504 (73984 L mol⁻¹ cm⁻¹).

Synthesis of BODIPY 3. 2,4-Dimethylpyrrole (0.7221 g, 7.6 mmol) and 4-(2-(trimethylsilyl)ethynyl)benzaldehyde (0.6060 g, 3.0 mmol) were dissolved in 90 mL of THF and stirred for 30 min under a N2 atmosphere. Then trifluoroacetic acid (2 drops) was added to the reaction mixture which was stirred for 12 h at room temperature. DDQ (0.7080 g, 3.1 mmol) was dissolved in 10 mL of THF and added dropwise within 25 min using a constant pressure dropping funnel. The reaction mixture solution was stirred at room temperature for 4 h and then placed in an ice bath. Triethylamine (18 mL) was added dropwise within 30 min. After being stirred for 5 min, boron trifluoride etherate (19 mL) was added dropwise to the reaction mixture which was stirred at room temperature for 12 h. The reaction mixture was extracted using DCM and water, the organic layer was dried by anhydrous Na₂SO₄. After filtration, the solvent was removed by evaporation. Then the mixture was purified by silica gel column chromatography using PE/DCM (4:1) as the eluent to give product $3^{45,46}$ as an orange powder (819.8 mg, 65%). ¹H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H, phenyl ring H), 7.24 (d, J = 8.4 Hz, 2H, phenyl ring H), 5.98 (s, 2H, pyrrole ring *H*), 2.55 (s, 6H, pyrrole ring *CH*₃), 1.39 (s, 6H, pyrrole ring CH_3 , 0.28 (s, 9H, Si(CH_3)₃).

Synthesis of BODIPY 4. Compound 3 (0.1263 g, 0.3 mmol) was dissolved in 5 mL of DCM and the mixture was stirred at room temperature under a N2 atmosphere. KOH (0.0842 g, 1.5 mmol) in 5 mL of methanol was added to the reaction mixture and the mixture was stirred at room temperature for 30 min. Then the mixture was extracted by DCM and H₂O, the organic layer was dried with anhydrous Na₂SO₄. After filtration, the solvent was removed in vacuo, and the mixture was purified by silica gel column chromatography using PE/DCM (4:1) as the eluent to give 4⁴⁶ in 81% yield (84.8 mg). ¹H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, I = 7.6 Hz, 2H, phenyl ring H), 7.27 (d, I =6.8 Hz, 2H, phenyl ring H), 5.99 (s, 2H, pyrrole ring H), 3.19 (s, 1H, alkynyl H), 2.56 (s, 6H, pyrrole ring CH₃), 1.40 (s, 6H, pyrrole ring CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 155.98, 143.11, 135.74, 133.87, 133.02, 128.80, 128.36, 123.09, 121.55, 83.02 (alkynyl C), 78.71 (alkynyl C), 14.76 (pyrrole ring CH₃), 14.73 (pyrrole ring CH_3); ¹⁹F-NMR (376 MHz, $CDCl_3$) δ -146.27 (q, J = 32.9 Hz); HRMS (MALDI-TOF) m/z calcd for $C_{21}H_{19}BF_2N_2 [M^+]$ 348.1608, found 348.1617.

Synthesis of BODIPY 5. Compound 4 (0.3491 g, 1.0 mmol), *p*-iodoaniline (0.2636 g, 1.2 mmol) and PPh₃ (0.1310 g, 0.5 mmol) were dissolved in 20 mL of toluene/Et₃N (3:1) in an oven-dried, 25 mL 2-neck flask equipped with a gas inlet adaptor under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature under a N₂ atmosphere for 30 min. $Pd_2(dba)_3$ (0.1830 g, 0.2 mmol) was added quickly.

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The reaction mixture was stirred at 60 °C for 72 h until 4 disappeared. After filtration, the solvent was removed. The mixture was purified by silica gel column chromatography using PE/DCM (1:4) as the eluent to give 5 in 67% yield (295.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 8.2 Hz, 2H, phenyl ring H), 7.36 (d, I = 8.5 Hz, 2H, phenyl ring H), 7.25 (d, J = 8.5 Hz, 2H, phenyl ring H), 6.66 (d, J = 8.5 Hz, 2H, phenyl ring H), 5.99 (s, 2H, pyrrole ring H), 3.87 (bs, 2H, NH), 2.56 (s, 6H, pyrrole ring CH_3), 1.43 (s, 6H, pyrrole ring CH_3); ¹³C NMR (100 MHz, CDCl₃) δ 155.77, 147.11, 143.22, 141.22, 134.34, 133.21, 132.16, 131.40, 128.20, 124.90, 121.43, 114.90, 112.15, 91.79 (alkynyl C), 86.83 (alkynyl C), 14.76 (pyrrole ring *C*H₃); ¹⁹F-NMR (376 MHz, CDCl₃) δ –146.24 (q, *J* = 32.9 Hz); FT-IR ν/cm^{-1} (KBr) 3410, 3034, 2955, 2922, 2855, 2208, 1626, 1600, 1548, 1523, 1509, 1470, 1409, 1307, 1264, 1196, 1156, 1084, 983, 831, 765, 707, 528, 477; HRMS (MALDI-TOF) m/z calcd for C₂₇H₂₄BF₂N₃ [M⁺] 439.2031, found 439.2040.

Synthesis of BODIPY 6. Compound 5 (0.4410 g, 1.0 mmol) and potassium carbonate (0.2020 g, 1.5 mmol) were dissolved in 1.5 mL of DMF in an oven-dried, 25 mL 2-neck flask equipped with a gas inlet adaptor under an atmosphere of nitrogen. The reaction was stirred under a N2 atmosphere at room temperature for 20 min. Then, ethyl bromoacetate $(135 \ \mu\text{L}, 1.2 \ \text{mmol})$ was added to the mixture using a syringe. After 10 min, the flask was equipped with an airproof stopper and stirred at 60 °C for 12 h and monitored by TLC. The solvent was removed in vacuo and the mixture was purified by silica gel column chromatography (PE/DCM, 1:3) giving 163.6 mg of 6 as an orange solid (31%). ¹H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.9 Hz, 2H, phenyl ring H), 7.32 (d, J = 8.3 Hz, 2H, phenyl ring H), 7.17 (d, J = 7.9 Hz, 2H, phenyl ring H), 6.50 (d, J =8.4 Hz, 2H, phenyl ring H), 5.91 (s, 2H, pyrrole ring H), 4.47 (t, J = 5.5 Hz, 1H, NHCH₂), 4.19 (q, J = 7.1 Hz, 2H, OCH₂CH₃), 3.85 $(d, J = 5.2 \text{ Hz}, 2H, \text{NHC}H_2)$, 2.48 (s, 6H, pyrrole ring CH₃), 1.36 (s, 6H, pyrrole ring CH_3), 1.23 (t, J = 7.2 Hz, 3H, OCH_2CH_3); $^{13}{\rm C}$ NMR (100 MHz, CDCl₃) δ 170.76 (C=O), 155.73, 147.34, 143.19, 141.22, 134.27, 133.20, 132.11, 131.38, 128.18, 124.93, 121.41, 112.76, 111.66, 91.86 (alkynyl C), 86.94 (alkynyl C), 61.66 (OCH₂CH₃), 45.48 (NHCH₂), 14.72 (pyrrole ring CH₃), 14.31 (OCH_2CH_3) ; ¹⁹F-NMR (376 MHz, CDCl₃) δ -146.23 (q, J = 32.9 Hz); FT-IR ν/cm^{-1} (KBr) 3405, 2962, 2924, 2855, 2208, 1738, 1610, 1600, 1546, 1527, 1509, 1469, 1408, 1374, 1309, 1195, 1158, 1083, 984, 833, 805, 765, 708, 477; HRMS (MALDI-TOF) m/z calcd for C₃₁H₃₀BF₂N₃O₂ [M⁺] 525.2399, found 525.2391.

Synthesis of C₆₀-B2. A solution of 6 (0.3630 g, 0.69 mmol), and C₆₀ (0.2271 g, 0.32 mmol) in ODCB (8 mL) was bubbled with N₂ for 1 h at room temperature. Then ethyl glyoxylate (315 μ L, 1.6 mmol) was added and the reaction mixture was heated to 170 °C for 4 h (monitored by TLC) with stirring. After the solvent was removed under reduced pressure, the mixture was purified by silica gel column chromatography using CS₂/ DCM (1:1) as the eluent to give C₆₀-B2 as a brown orange powder (104.8 mg, 25%). ¹H NMR (400 MHz, CDCl₃) δ 7.70–7.66 (m, 4H, phenyl ring *H*), 7.32–7.29 (m, 4H, phenyl ring *H*), 6.56 (s, 2H, CHCO₂), 6.01 (s, 2H, pyrrole ring *H*), 4.34–4.22 (m, 4H, OCH₂CH₃), 2.57 (s, 6H, pyrrole ring CH₃), 1.46 (s, 6H, pyrrole

ring CH_3), 1.19 (t, J = 7.1 Hz, 6H, OCH_2CH_3); ¹³C NMR (100 MHz, CDCl₃) δ 170.11 (C=O), 155.87, 153.21, 150.24, 147.69, 146.63, 146.58, 146.31, 146.00, 145.96, 145.83, 145.74, 145.69, 145.53, 145.47, 144.71, 144.64, 143.30, 143.18, 142.96, 142.88, 142.39, 142.33, 142.12, 142.03, 141.99, 141.88, 141.03, 140.39, 139.83, 136.94, 136.24, 134.87, 133.20, 132.37, 131.37, 128.34, 124.45, 121.49, 118.70, 116.33, 90.88 (alkynyl C), 88.44 (alkynyl C), 74.45 (CHCO₂), 71.08 (sp^3 -C of C₆₀), 62.26 (OCH₂CH₃), 14.80 (pyrrole ring CH₃), 14.35 (OCH₂CH₃); ¹⁹F-NMR (376 MHz, CDCl₃) δ -146.25 (q, J = 32.9 Hz); FT-IR ν/cm^{-1} (KBr) 2953, 2921, 2851, 1735, 1600, 1542, 1509, 1463, 1409, 1368, 1308, 1189, 1156, 1084, 981, 833, 765, 707, 577, 526; HRMS (MALDI-TOF) m/z calcd for $C_{95}H_{34}BF_2N_3O_4$ [M^{•-}] 1329.2616, found 1329.2601; UV-vis (toluene) λ_{max}/nm 317 $(74153 \text{ L} \text{mol}^{-1} \text{ cm}^{-1}), 431 (5143 \text{ L} \text{mol}^{-1} \text{ cm}^{-1}), 477$ $(18\,699 \text{ Lmol}^{-1} \text{ cm}^{-1}), 505 (73\,984 \text{ Lmol}^{-1} \text{ cm}^{-1}).$

Results and discussion

Synthesis and structural characterization

The strategy employed for the preparation of C_{60} -B1 and C_{60} -B2 is based on 1,3-dipolar cycloaddition of the azomethine ylide to C_{60} .⁴⁷ The synthesis procedures are shown in Scheme 1.

BODIPY **1** was synthesized from *p*-nitrobenzaldehyde and 2,4-dimethyl-1*H*-pyrrole in a one-pot reaction with dry THF as the solvent.⁴⁴ The reduction of **1**⁴⁴ with NH₂NH₂·H₂O using Pd/C as the catalyst in ethanol under an argon atmosphere at 100 °C for 2 h gave **R1**⁴⁴ in 95% yield. Nucleophilic substitution of **R1** with ethyl bromoacetate using K₂CO₃ as a base in DMF at 60 °C for 9 h provided **2** in 82% yield. Finally, the dyad **C**₆₀-**B1** was obtained in 30% yield by 1,3-dipolar cycloaddition of **2** with glyoxylic acid ethyl ester and C₆₀ in *o*-dichlorobenzene (ODCB) at 170 °C for 4 h.

Compound $3^{45,46}$ was synthesized following a similar procedure as **1**. Deprotection of the trimethylsilyl (TMS) group in **3** using KOH produced 4^{46} in 81% yield. The cross-coupling reaction of **4** with *p*-iodoaniline furnished **5** in 67% yield. Then **5** was allowed to react with ethyl bromoacetate at 60 °C for 12 h to provide **6** in 31% yield. Finally, **1**,3-dipolar cycloaddition of the azomethine ylide to C₆₀ afforded the dyad **C**₆₀-**B2** in 25% yield. **R2** was prepared and used as per ref. 43.

The structures of all the compounds were established by NMR, mass and IR spectroscopy techniques. The ¹H NMR spectra of C_{60} -B1 and C_{60} -B2 in CDCl₃ give all the expected signals. For example, single peaks at 6.02 ppm for protons of the pyrrole ring, and peaks at 2.54 ppm and 1.47 ppm assigned to the protons of methyl groups correspond to the BODIPY skeleton protons. A singlet at 6.57 ppm for both C_{60} -B1 and C_{60} -B2 is assigned to methine protons of the pyrrolidine ring. No more than 28 peaks in the 136–154 ppm range for the sp²-carbons of the C_{60} cage and one peak at ~71 ppm for the sp³-carbons of the C_{60} -B1 and C_{60} -B2, which is in line with the C_2 symmetry of the two compounds. Quartet peaks at ~146 ppm in the ¹⁹F-NMR spectra of 2, 4, 5, 6, C_{60} -B1 and C_{60} -B2 indicate



that the BODIPY cores are intact. The IR spectra of C_{60} -B1 and C_{60} -B2 show characteristic absorption of C_{60} and the BODIPY skeleton. The mass spectra of C_{60} -B1 and C_{60} -B2 give molecular peaks at m/z 1229.2302 and 1329.2601, respectively.

Steady state UV-vis absorption and fluorescence spectra

The UV-vis absorption spectra of R1, R2, C₆₀-B1 and C₆₀-B2 were recorded in toluene and are shown in Fig. 2a. R2 with only a C₆₀ monomer shows weak absorption in the visible range, and only a weak absorption peak at 430 nm with molar extinction coefficient ε equaling 7124 L mol⁻¹ cm⁻¹ could be found. R1, C₆₀-B1 and C₆₀-B2 containing the BODIPY unit show a strong absorption peak at about 503 nm (with molar extinction coefficients approximately equal to 73 908 L mol⁻¹ cm⁻¹) and a weak absorption around 475 nm. Compared with R1, the maximum absorption peaks of C60-B1 and C60-B2 are redshifted by about 2 nm and 3 nm, respectively. The UV-vis spectrum of C₆₀-B1 is essentially superimposition of C₆₀ and BODIPY units. Due to the introduction of the phenylethynyl group in C₆₀-B2, a large and wide absorption peak appears at 318 nm (ε = 74 487 L mol⁻¹ cm⁻¹). The absorption spectra of both C60-B1 and C60-B2 feature bands at essentially the same



Fig. 2 (a) UV-vis absorption spectra of C₆₀-B1, C₆₀-B2, R1 and R2 in toluene ($c = 1.0 \times 10^{-5} \text{ mol L}^{-1}$). (b) Fluorescence of C₆₀-B1, C₆₀-B2, R1 and R2 in toluene (excited at 485 nm, $c = 1.0 \times 10^{-5} \text{ mol L}^{-1}$). The inset shows the local magnified fluorescence emission intensity.

positions as their monomers, suggesting that at the ground state the molecular orbitals are independent from each other.

The fluorescence spectra of C₆₀-B1, C₆₀-B2, R1 and R2 in toluene are shown in Fig. 2b. When excited at 485 nm, R1, C60-B1 and C60-B2 exhibit similar spectral characteristics corresponding to the BODIPY unit. Compared with R1, the luminescence intensities of C60-B1 and C60-B2 at approximately 520 nm are largely quenched due to energy transfer^{8,20} or electron transfer^{19,48} upon photoexcitation. The luminescence quenching efficiency for C_{60} -B2 is determined to be ~94% relative to the reference BODIPY monomer. In the magnified spectra of Fig. 2b, a more weak fluorescence emission at 520 nm for C₆₀-B1 suggests a more efficient quenching of the BODIPY fluorescence in this dyad. The fluorescence quenching of approximately 99% is detected in C₆₀-B1. The more profound quenching of the BODIPY fluorescence in C60-B1 indicates that the shorter distance between C₆₀ and BODIPY leads to higher efficiency of energy transfer or electron transfer.³⁵ The S₁ state of C_{60} (1.72 eV) is lower than that of BODIPY (2.4 eV); thus the intramolecular energy transfer from the BODIPY to C₆₀ unit is possible.16,30

Time-resolved fluorescence spectroscopy

To investigate the effect of the bridge length between C_{60} and BODIPY on energy transfer of C_{60} -B1 and C_{60} -B2, the fluorescence decays of these compounds were measured *via* timecorrelated single photon counting (TCSPC). The fluorescence decay curves recorded for C_{60} -B1, C_{60} -B2 and R1 at 520 nm due to the BODIPY emission exhibit monoexponential decays as shown in Fig. 3 and Fig. S1 (ESI†), respectively. Both the lifetimes of C_{60} -B1 (τ is less than 0.1 ns) and C_{60} -B2 ($\tau = 0.18$ ns) are much shorter than that of R1 ($\tau = 1.84$ ns), indicating an effective excitation energy quenching of the BODIPY unit by C_{60} . Furthermore, a shorter lifetime of C_{60} -B1 compared to C_{60} -B2 suggests that a shorter bridge between C_{60} and BODIPY results in more effective excitation energy transfer, which is consistent with the emission decrease observed in the steady-state spectra.



Fig. 3 Fluorescence decay traces obtained with TCSPC of (a) **C**₆₀-**B1** and (b) **C**₆₀-**B2** in toluene (1 × 10⁻⁶ mol L⁻¹) and the results of single exponential function-fitting combining a deconvolution (ex 475 nm, em 520 nm).

In addition, from the kinetics measurement, the excitation deactivation rate of the BODIPY moiety can be calculated using $k_0 = 1/\tau_0$, and that of **C**₆₀-**B1** could be determined by $k_0 + k_1 = 1/\tau_1$, where k_1 is the energy transfer rate constant from BODIPY to C₆₀. The energy transfer efficiency of **C**₆₀-**B1**, Φ_1 , could be determined by using eqn (1).

$$\Phi_1 = \frac{k_1}{(k_0 + k_1)} = \frac{1/\tau_1 - 1/\tau_0}{1/\tau_1} \tag{1}$$

where $\tau_0 = 1.84$ ns and $\tau_1 > 0.1$ ns; thus $\Phi_1 > 0.95$ could be obtained. In the same way, the energy transfer efficiency Φ_2 is determined as ~0.90 for C₆₀-B2. Both Φ_1 and Φ_2 are in consistence with those obtained from the steady-state spectra mentioned before.

TD-DFT calculations

The molecular structure optimization and TD-DFT calculations were conducted at the CAM-B3LYP/3-21G level to gain insight into the excited-state properties of the dyads. The charge difference densities (CDDs) of the Franck–Condon state and the lowest excited states of C_{60} -B1 and C_{60} -B2 are shown in Fig. 4.⁴⁹ In the TD-DFT calculations, the CDD profile describes the holes (green) and electrons (red) distribution on atoms at excited states. Although energy transfer or electron transfer are possible from BODIPY to C_{60} ,^{16,50} the CDDs for both C_{60} -B1 and C_{60} -B2 do not exhibit significant charge separation. The profile migration from BODIPY to the C_{60} moiety indicates an

Energy

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Energy

intramolecular energy transfer between them.⁸ In view of this, the emission quenching in the steady-state fluorescence spectra should be ascribed to energy transfer rather than electron transfer.

Nanosecond time-resolved transient absorption spectroscopy

The results of steady and transient fluorescence experiments indicate that the intramolecular energy transfer from BODIPY to the C_{60} unit produce the singlet excited state of C_{60} . As is well known, because of the conjugated π -network covering the entire molecular surface, C60 possesses high ISC efficiency, which results in a high triplet state yield (~ 1).^{17,18} In order to investigate the effect of bridge length on the production of triplet C₆₀ upon photoexcitation, nanosecond time-resolved transient absorption spectroscopy of the compounds was studied, and the results are illustrated in Fig. 5. According to the pulsed laser excitation of C60-B1 and C60-B2 at 532 nm, only typical transient absorption bands at 370 and 700 nm ascribed to the triplet excited state of C_{60} (as compared with the transient absorption bands of R2 and R1 in Fig. S2 in the ESI[†]) are observed. It should be pointed out that the T_1 state is exclusively located at the C60 unit rather than the BODIPY moiety, because no ground state bleaching band of the BODIPY moiety at 505 nm is observed. Therefore, the production of triplet excited states with the dyads is mainly attributed to the excitation of the BODIPY moiety and the intramolecular energy transfer from BODIPY to C₆₀ and the following ISC of C₆₀.

In addition, the Δ OD at 700 nm for C_{60} -B1 is higher than that for C_{60} -B2 at the same delay time and the signal enhancement in C_{60} -B1 is 1.4 times as that in C_{60} -B2. Since the initial concentration of the two dyads and the measurement conditions are identical, the higher Δ OD suggests that the yield of the triplet C_{60} moiety in C_{60} -B1 is relatively higher than that in C_{60} -B2. Here, the higher yield of the triplet C_{60} is ascribed to the shorter bridge in C_{60} -B1, because the excited state energy transfer from BODIPY to C_{60} is dependent on the distance between them, *i.e.* the shorter the distance, the higher the transfer rate, which will lead to more triplet C_{60} . Note that, although the triplet C_{60} amounts (Δ ODs) for both C_{60} -B1 and C_{60} -B2 are different, their triplet decay rate is identical since they all arise from the C_{60} moiety.

Singlet oxygen production





Fig. 4 CDDs of the Franck–Condon state and the lowest excited states of (a) C_{60} -B1 and (b) C_{60} -B2. The negative density (green) corresponds to holes and the positive (red) to electrons.

Fig. 5 Nanosecond time-resolved transient absorption spectra of (a) C_{60} -B1 and (b) C_{60} -B2 in deaerated toluene upon excitation (532 nm) at room temperature. Insets show the dynamic curves at 700 nm.

(a) Ex 532 nm

Ex 532 nm



Fig. 6 (a) Mechanism for photooxidation of DHN with photosensitizer (PS). Absorption spectral evolution for the photooxidation of DHN using (b) C₆₀-B1 and (c) C₆₀-B2 as sensitizers. (d) Plots of ln(A/A_0) vs. irradiation time for the photooxidation of DHN with different sensitizers (collected at 301 nm) in DCM/MeOH (9:1, v/v). c[sensitizers] = 1.0×10^{-5} mol L⁻¹, and c[DHN] = 1.0×10^{-4} mol L⁻¹.

scavenger, and the reaction mechanism for photooxidation of DHN with triplet photosensitizer is outlined in Fig. 6a. Production of ${}^{1}O_{2}$ can be monitored by following the decrease of the absorption of DHN at 301 nm with time.¹⁸ The spectral responses of DHN using C₆₀-B1, C₆₀-B2, the reference compounds (R1, R2), and MB as the sensitizers upon photoirradiation at 500 nm are presented in Fig. 6 and Fig. S3 (ESI⁺), respectively. To confirm the singlet oxygen generation of photosensitizer, the photo-oxidation of DHN without photosensitizer has been carried out as a control experiment and the data are shown in Fig. 6d and Fig. S3a (ESI[†]). No obvious UV-vis absorption change is observed in the spectral responses of DHN without photosensitizer. The spectral responses of DHN with C_{60} -B1 and C_{60} -B2 as sensitizers (Fig. 6b and c) exhibit remarkable UV-vis absorption change within the time-scale. The spectral alteration mentioned above is caused by the photooxidation of DHN instead of photobleaching, because no bleaching is observed for both C60-B1 and C60-B2 after being exposed to light for 1 h during the photostability measurement (see Fig. S4, ESI[†]). Compared with R1 and R2, the photooxidation

Table 1 The photooxidation rate constant and quantum yield of singlet oxygen of the sensitizers^a

	$k_{obs}{}^b/min^{-1}$	ν_{i}^{c}	$\Phi_{\scriptscriptstyle A}{}^d$
C ₆₀ -B1	14.7	1.47	0.82
C ₆₀ -B2	10.7	1.07	0.59
R1	3.4	0.34	—
R2	4.9	0.49	0.76^{e}
MB	11.4	1.14	0.57

^{*a*} In DCM/CH₃OH = 9:1 (v/v). $c = 1.0 \times 10^{-5}$ mol L⁻¹. ^{*b*} The rate constant $k_{\rm obs}$ was calculated by the rule: $\ln(A/A_0) = -k_{\rm obs}t$. In 10^{-3} min⁻¹. *A* and A_0 were the absorbance at 301 nm. ^{*c*} Initial consumption rate of DHN, $\nu_1 = k_{\rm obs}$ [DHN]. In 10^{-6} M min⁻¹. ^{*d*} Quantum yield of singlet oxygen (¹O₂), with MB as standard ($\Phi_A = 0.57$ in DCM). ^{*e*} Literature values.¹⁷

of DHN with C_{60} -B1 and C_{60} -B2 is more significant, which should be attributed to the energy transfer from BODIPY to C_{60} followed by the highly efficient ISC of C_{60} .

Fig. 6d shows the kinetics of photooxidation of the sensitizers, where C_{60} -B1 presents the highest photooxidation efficiency. The photooxidation rate constant and yield of singlet oxygen of the dyads are calculated¹⁸ and the data are listed in Table 1. The photooxidation rate constant (k_{obs}) of C_{60} -B1 (14.7 × 10⁻³ min⁻¹) is 1.4 times as that of C_{60} -B2 (10.7 × 10⁻³ min⁻¹) and 1.3 times as that of MB (11.4 × 10⁻³ min⁻¹). Due to the weak absorption of C_{60} in the visible range, R2 shows much slower photooxidation kinetics. Among all the investigated sensitizers, C_{60} -B1 gives the highest yield of singlet oxygen.

The formation of triplet excited states of the dyads includes four steps: the excitation of the BODIPY moiety, energy transfer to singlet C_{60} , ISC of C_{60} and backward triplet energy transfer from C_{60} to BODIPY.^{14,27} We failed to observe the triplet excited state of BODIPY, thus the fourth step does not exist in the dyads. Because the excitation of the BODIPY moiety and the ISC process for C_{60} in the dyads are identical, the discrepancy of singlet oxygen generation between C_{60} -B2 and C_{60} -B1 should be ascribed to the energy transfer from BODIPY to C_{60} . According to the data of the steady and kinetic spectra, the shorter bridge in C_{60} -B1 results in higher energy transfer efficiency in comparison with that of C_{60} -B2. As a result, C_{60} -B1 can generate higher yield of the triplet C_{60} and singlet oxygen during equal periods of time.

Conclusions

In summary, the effect of bridge length on singlet oxygen generation of triplet photosensitizers has been studied by synthesizing two C60-BODIPY dyads with different bridge lengths: C60-B1 (with benzene as the bridge) and C60-B2 (using diphenylacetylene as the bridge). Both dyads are axially symmetrical with rigid bridges, ensuring a relatively constant spatial distance between BODIPY and C₆₀. According to the calculated data, the bridge length of C₆₀-B2 is about 6.9 Å longer than that of C₆₀-B1. Steady-state and time-resolved fluorescence spectra indicate that C60-B1 with a shorter bridge shows more effective energy transfer compared to C60-B2. Moreover, the results of the nanosecond time-resolved transient absorption spectroscopy confirm that the yield of the triplet C₆₀ moiety in C₆₀-B1 is 1.4 times that in C₆₀-B2. The photooxidation reactions of DHN demonstrate that the two dyads exhibit significantly enhanced photooxidation efficiencies in comparison with single BODIPY or C60. C60-B1 with a shorter bridge generates a higher yield of singlet oxygen than C₆₀-B2. The photooxidation rate constant of C₆₀-B1 is 1.4 times as that of C_{60} -B2 and 1.3 times as that of MB. In conclusion, the results obtained here can offer a useful strategy to design new triplet photosensitizers for potential application in photovoltaics, photodynamic therapy and other photoelectric fields.

Conflicts of interest

There are no conflicts to declare.

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