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Introduction

Modulation of the singlet/triplet excited state of chromophores is important for photocatalysis,^{1–3} molecular valves,^{4,5} molecular memory devices,⁶ chemical or biological sensors⁷ and controllable photodynamic therapy (PDT),^{8–13} *etc.* On the other hand, modulation of singlet/triplet excited state of chromophores will present an additional dimension to the application of fluorophores in various areas. For example, modulation of the excited state of chromophores with an external-stimuli responsive unit in the multi-chromophore molecules will lead to functional compounds, such as fluorescent molecular probes,^{14–17} and activatable PDT reagents.^{4,18–20} Concerning these aspects, ferrocene (Fc) is of particular interest due to its redox centre which

Preparation of Bodipy–ferrocene dyads and modulation of the singlet/triplet excited state of bodipy *via* electron transfer and triplet energy transfer[†]

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Modulation of the singlet/triplet excited state of a fluorophore is becoming more important for molecular switches, molecular memory devices, chemical or biological sensors and controllable photodynamic therapy (PDT) *etc.* Boron-dipyrromethene (Bodipy)–ferrocene (Fc) dyads were prepared for reversible electrochemical switching of the singlet excited state (fluorescence), as well as the triplet excited states of Bodipy. The photophysical properties of the dyads were studied using steady-state UV-vis absorption spectroscopy, fluorescence, electrochemical characterization, time-resolved fluorescence and nanosecond transient absorption spectroscopies. The fluorescence of the Bodipy moieties in the dyads was quenched significantly, due to the photo-induced electron transfer (PET). This conclusion was supported by electrochemical characterization and calculation of the Gibbs free energy changes of PET. We demonstrated that the fluorescence of the Bodipy moiety can be reversibly switched ON and OFF by electrochemical oxidation of the Fc moiety (Fc/Fc⁺). Furthermore, we proved that the Fc moiety is efficient for quenching of the triplet excited states of Bodipy. Two quenching mechanisms, PET and triplet-triplet-energy transfer (TTET), are responsible for the intramolecular and intermolecular quenching of the triplet excited states of Bodipy.

displays an outstanding reversible redox behaviour and its electrondonating ability which can be modulated by electrochemical oxidation reversibly. Fc has been extensively used for studying the electron transfer in molecular dyads and triads, as well as in controlling the fluorescence *via* photo-induced electron transfer (PET).^{21,22} For example, previously it was shown that Fc is a strong electron donor in the Fc-Bodipy–C₆₀ triad, in the PET process.²³ The Fc-Bodipy dyad was used as a viscosity probe, the quenching mechanism was attributed to the free rotor effect.²⁴ However, the quenching effect of Fc on the triplet excited state of organic chromophores, especially those show strong absorption of visible light and long-living triplet state, was rarely studied.^{21,22}

Previously the quenching of the triplet excited state of organic chromophores by Fc *via* intermolecular triplet energy transfer (EnT) or electron transfer (ET) was studied.²⁵ But the triplet state energy donors studied were limited to the polycyclic aromatic hydrocarbons, such as anthracene and naphthalene, *etc.*²⁵ The photophysics of the Fc-perylenediimide (PDI) dyad and triads was studied, PET with Fc as the electron donor was confirmed from the femtosecond transient absorption spectra, and it was found that the triplet state of the PDI moiety was formed by charge recombination (CR).²⁶ The photo-induced intramolecular ET was studied with the C₆₀-Fc dyad.²⁷ Ultrafast photo-induced charge separation and electron transfer were

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Scheme 1 (a) Acetyl chloride and AlCl₃, DCM, 25 °C, Ar, 30–60 min; yield 75.3%; (b) POCl₃/DMF, 0 °C, Ar, 1.5 h. NaOAc, 25 °C, Ar, 1 h; yield 76.3%; (c) 1,4-dioxane, NaOH, reflux, 0.5 h; yield 90.7%; (d) HgOAc, MeOH/benzene, 25 °C, Ar, 12 h; (e) LiCl, EtOH–H₂O mixture, 25 °C, Ar, 1 h; yield 60.8%; (f) NIS, dry DCM, 0 °C, Ar, 12 h; NaHSO₃; yield 74.7%; (g) Ar, DCM, TFA, DDQ, Et₃N and BF₃-Et₂O; (h) NIS, dry DCM, 25 °C, Ar, 12 h; (i) Pd(PPh₃)₂Cl₂, PPh₃, Cul, THF, NEt₃, Ar, 90 °C, 8 h; (j) sodium ascorbate, CuSO₄, 25 °C, Ar, 60 h.

reported using the C_{60} -NDI–Fc triad (NDI = naphthalenediimide).²⁸ The photoinduced electron transfer in the Fc–azaBodipy dyad and triad was studied, but the azaBodipy part in the dyad and triad is unable to produce a triplet excited state efficiently.²⁹ To the best of our knowledge, the effect of the Fc moiety on the triplet excited state of the visible light-harvesting organic chromophores was not studied.²¹

Herein we prepared Fc-Bodipy and Fc-diiodoBodipy dyads with different linkers between the two chromophores in the dyads (B-1, B-2 and B-3. Scheme 1), with the aim to study the modulation effect of Fc on the singlet excited state and the triplet excited state of Bodipy. To the best of our knowledge, this is the first time that controlling of the triplet excited state of Bodipy by Fc was studied. Furthermore, we switched the fluorescence of the Bodipy chromophore via reversible redox manipulation of the Fc unit in the dyads. The photophysical properties of the Fc-Bodipy and Fc-diiodobodipy dyads were studied using steady-state UV-vis absorption spectroscopy, fluorescence spectroscopy, spectroelectrochemistry and nanosecond transient absorption spectroscopy. The intermolecular electron and energy transfer processes were studied. We found that the fluorescence of the Bodipy can be reversibly switched by electrochemical oxidation and reduction of the Fc moiety (via a spectroelectrochemical method), and the triplet excited state of the 2,6-diiodoBodipy moiety can be quenched by both the electron transfer and triplet-triplet energy transfer (TTET) processes.

Experimental section

Analytical measurements

All the chemicals were analytically pure and were used as received. Solvents were dried and distilled prior to use. 1 H and 13 C NMR

spectra were recorded using a Bruker 400/500 MHz spectrophotometer (CDCl₃ as solvent, TMS as standard for which δ = 0.00 ppm). High resolution mass spectra (HRMS) were determined using a MALDI-HRMS, ESI-Q-TOF MS spectrometer.

Synthesis of complex B-1

Under an Ar atmosphere, a mixture of 7 (1.91 g, 10 mmol) and 2,4-dimethylpyrrole (1.88 g, 20 mmol) in dry CH₂Cl₂ (250 mL) was stirred at rt. Then TFA (0.1 mL) was added into the mixture using a syringe and the mixture was stirred at RT overnight. DDQ (1.13 g, 5 mmol) was dissolved in dry CH₂Cl₂ (30 mL) and the solution was poured into the mixture in one portion, then the mixture was stirred at RT for 7 h. Triethylamine (10 mL) was added dropwise into the mixture with cooling using an ice bath. The reaction mixture was stirred for another 0.5 h. Then BF₃. Et₂O (10 mL) was added dropwise into the mixture. The reaction mixture was stirred overnight. The solution was concentrated under reduced pressure and water (200 mL) was added. The mixture was stirred for 24 h. Then the solution was extracted with CH_2Cl_2 (3 × 100 mL) and the organic layer was dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, CH_2Cl_2 /petroleum ether = 1:1, v/v) to give **B-1** as a red solid. Yield: 300 mg (7.5%). M.p. 146.5–148.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, J = 12.0 Hz, 2H), 7.05 (d, J = 12.0 Hz, 2H), 5.98 (s, 2H), 4.21 (t, J = 4.0 Hz, 2H), 3.67 (t, J = 4.0 Hz, 2H), 2.55 (s, 6H), 1.43 (s, 6H). MALDI-HRMS: m/zcalcd for $[C_{21}H_{22}N_5OBF_2]^+$ 409.1885; found: m/z = 409.1859.

Synthesis of complex B-2

To a solution of **B-1** (200 mg, 0.49 mmol) in anhydrous CH_2Cl_2 (25 mL) was added *N*-iodosuccinimide (NIS, 558 mg, 2.48 mmol).

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The mixture was stirred at 30 °C overnight. The reaction mixture was concentrated under vacuum, and the residue was purified by column chromatography (silica gel. petroleum ether/CH₂Cl₂ = 2:1, v/v). The red band was collected, and the solvent was removed under reduced pressure to give the product as a red solid. Yield: 280.0 mg (90.4%). M.p. 168.7–170.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 4.24 (t, *J* = 4.0 Hz, 2H), 3.69 (t, *J* = 4.0 Hz, 2H), 2.65 (s, 6H), 1.45 (s, 6H). MALDI-HRMS: *m/z* calcd for [C₂₁H₂₀N₅OBF₂I₂]⁺ *m/z* = 660.9804; found: *m/z* = 660.9817.

Synthesis of complex B-3

Under an Ar atmosphere, to a solution of 4-ethynylbenzaldehyde 8 (400.0 mg, 3.0 mmol) and 2,4-dimethylpyrrole (672 mg, 7.0 mmol) in CH₂Cl₂ (250 mL) was added trifluoroacetic acid (2.3 mL, 0.034 mmol). The mixture was stirred at RT for 1 h then p-chloranil (756.0 mg, 3.0 mmol) was added. The mixture was stirred at RT for another 1 h. NEt₃ (5.26 g, 52.0 mmol, 7.2 mL) was added, and the mixture was stirred for 10 min. Then BF₃·OEt₂ (8.02 g, 55.3 mmol) was added via a syringe and the mixture was stirred for another 10 min. The reaction mixture was washed with water (4 \times 60 mL) and dried with anhydrous Na₂SO₄. The solvent was removed under vacuum and the residue was purified by chromatography (silica gel, petroleum ether/ $CH_2Cl_2 = 1:1, v/v$) to give compound B-3 as an orange solid. Yield: 320 mg (28.9%). M.p. 243.1–245.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 5.99 (s, 2H), 3.18 (s, 1 H), 2.56 (s, 6H), 1.40 ppm (s, 6H). TOF HRMS EI⁺: calcd [C₂₁H₁₉BN₂F₂] m/z = 348.1609; found, m/z = 348.1617.

Synthesis of complex FcB-0

Under an Ar atmosphere, ethylnylferrocene (21.0 mg, 0.1 mmol) and 3 (20 mg, 0.1 mmol) were dissolved in a mixed solvent CHCl₃/MeOH/H₂O (8 mL, 6:1:1, v/v). Then CuSO₄·5H₂O (7.5 mg) and sodium ascorbate (11.5 mg) were added. The resulting mixture was stirred at 25 °C for 16 h. Then the reaction mixture was washed with water and extracted with CH₂Cl₂ (3 × 50 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, CH₂Cl₂) to give a red solid. 18.0 mg, yield: 43.9%. M.p. 132.5–134.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 1H), 7.32 (t, *J* = 16 Hz, 2H), 7.01 (t, *J* = 16 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.78 (t, *J* = 8.0 Hz, 2H), 4.72 (s, 2H), 4.40 (t, *J* = 8.0 Hz, 2H), 4.30 (s, 2H), 4.07 (s, 5H). TOF HRMS EI⁺: calcd [C₂₀H₁₉N₃OFe] *m*/*z* = 373.0878, found, *m*/*z* = 373.0871.

Synthesis of complex FcB-1

Complex **FcB-1** was prepared by a similar procedure to that used for complex **FcB-0**, with ethylnylferrocene (21.0 mg, 0.1 mmol) and **B-1** (44 mg, 0.1 mmol) as the starting materials, instead of **3**. Complex **FcB-1** was obtained as a red solid 48.0 mg, yield: 77.4%. M.p. 211.8–212.6 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.57(s, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 5.96 (s, 2H), 4.98 (s, 2H), 4.78 (s, 2H), 4.54 (s, 2H), 4.42 (s, 2H), 4.25 (s, 5H), 2.54 (s, 6H), 1.39

(s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 158.45, 155.47, 154.20, 147.06, 143.07, 141.09, 131.73, 129.54, 128.22, 121.20, 115.12, 111.23, 99.96, 91.17, 66.75, 57.93, 50.33, 14.69, 14.59. MALDI-HRMS: *m*/*z* calcd for [C₃₃H₃₂N₅OBF₂Fe]⁺ *m*/*z* = 619.2017; found: *m*/*z* = 619.2028.

Synthesis of complex FcB-2

Complex **FcB-2** was prepared by a similar procedure to that used for complex **FcB-1**, with ethylnylferrocene (21.0 mg, 0.1 mmol) and **B-2** (66 mg, 0.1 mmol) as the starting materials, instead of **B-1**. Complex **FcB-1** was obtained as a deep red solid 65.3 mg, yield: 73.6%. M.p. 235.8–237.6 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.81 (t, *J* = 8.0 Hz, 4H), 4.46 (t, *J* = 8.0 Hz, 2H), 4.39 (s, 2H), 4.13 (s, 5H), 2.63 (s, 6H), 1.39 (s, 6H). ¹³CNMR (100 MHz, CDCl₃) δ = 158.78, 156.86, 145.47, 141.06, 131.68, 129.72, 127.96, 116.65, 106.58, 96.08, 85.66, 68.84, 52.91, 29.50, 18.02, 16.09. MALDI-HRMS: *m/z* calcd for [C₃₃H₃₀N₅OBF₂FeI₂]⁺ *m/z* = 870.9950; found: *m/z* = 870.9945.

Synthesis of complex FcB-3

Iodoferrocene (62.4 mg, 0.2 mmol) was added to a deaerated solution of B-3 (69.6 mg, 0.2 mmol) in THF (15 mL) and triethylamine (5 mL) (deoxygenated by Ar for 15 min). After the mixture was stirred for 10 min, [PdCl₂(PPh₃)₂] (14.0 mg, 0.02 mmol) and CuI (3.8 mg, 0.02 mmol) were added into the solution, then the mixture was refluxed for 8 h. After cooling to RT, the reaction mixture was poured into water, and the aqueous phase was extracted with CH₂Cl₂ (50 mL). The combined organic extracts were washed with water (50 mL) and then brine (50 mL) and dried over anhydrous Na₂SO₄. The mixture was filtered, concentrated under reduced pressure, and purified by chromatography (silica gel; CH₂Cl₂/petroleum ether = 1/4, v/v) to give a deep-red solid. Yield: 30.4 mg (28%). ¹H NMR (400 Mz, CDCl₃) δ 7.62 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 4.0 Hz, 2H), 5.99 (s, 2H), 4.53 (t, J = 4.0 Hz, 2H), 4.28 (s, 7H), 2.56 (s, 6H), 1.44 (s, 6H). MALDI-HRMS: calcd $[C_{31}H_{27}BF_2 FeN_2]^{\dagger}$ m/z = 532.1585, found, m/z = 532.1611.

Nanosecond time-resolved transient difference absorption spectroscopy

The nanosecond time-resolved transient absorption spectra were recorded on an LP920 laser flash photolysis spectrometer (Edinburgh Instruments, UK). The samples were excited using a nanosecond pulsed laser (Opotech, wavelength tunable in the range of 410–2400 nm), and the transient signals were recorded on a Tektronix TDS 3012B oscilloscope. All samples in flash photolysis experiments were deaerated with nitrogen for *ca.* 15 min before measurement.

Spectroelectrochemical studies

Spectroelectrochemical fluorescence measurements were performed using a spectro-electrochemical quartz cell (path-length of 1.0 mm) with a three-electrode system: light transparent platinum gauze (100 mesh, 7.0×5.0 mm) as a working

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electrode, a platinum wire a counter electrode, and an Ag wire reference electrode. Potentials were applied using a CHI610d electrochemical workstation. The electrochemical reaction was monitored using a RF5301PC spectrofluorometer (Shimadzu, Japan). All electrochemical measurements were carried out under a nitrogen atmosphere.

Results and discussion

Design and synthesis of the Fc-Bodipy dyads

Due to the intense visible light absorption, high fluorescence quantum yields and feasible derivatization,^{16,30–33} boron dipyrromethene (BODIPY) was selected as the organic chromophore. Ferrocene, the strong electron donor in the PET process, was selected to tune the singlet and triplet excited states of organic chromophores. The linker between Fc and Bodipy could greatly influence the electron and energy transfer, so various linkers, e.g. acetylide and 1,2,3-triazole, were firstly used in dyads FcB-1 and FcB-3 to tune the quenching effect of Fc on the singlet excited state of organic chromophores (Scheme 1), which benefits the subsequent study of the quenching effect on triplet excited states. Compared with acetylide connection, 1,2,3-triazole shows a moderate electron transfer rate (vide infra), which benefits the study about the quenching effect of electron and energy transfer on the triplet excited state of organic chromophores, respectively. Thus FcB-2 was devised, wherein 1,2,3-triazole connects the Fc and the 2,6-diiodoBodipy parts together (Scheme 1). Compounds B-1, B-2 and B-3 were prepared as references for the study of the photophysical properties of the dyads (Scheme 1). All the compounds were obtained with moderate to satisfactory yields. The molecular structures were fully verified using ¹H NMR, ¹³C NMR and HRMS spectra. Compounds 1, 2, 3, 5, 6, 7, 8 were

synthesized according to previously reported methods (see ESI† for synthesis and molecular structural characterization data).

Steady-state electronic spectroscopy (UV-vis absorption and emission spectra)

The UV-Vis absorption spectra of the compounds were studied (Fig. 1). Fc as the electron donor moiety in Fc-Bodipy dyads does not show any significant absorption in the visible region, while Bodipy shows intense absorption in the visible region. For FcB-1, it shows similar absorption to that of the reference compound B-1, especially in the visible spectral region (Fig. 1a). This result indicates that there is no significant electronic interaction between the Fc and the Bodipy moieties in FcB-1 in the ground state. Similar results were observed for FcB-2 and FcB-3 (Fig. 1b and c). The UV-Vis absorption spectra of compounds do not show significant solvent dependency (see ESI,† Fig. S31 and S32), further indicating that the ground state was not affected by the solvent polarity or hydrogen bonding. Actually, these dyads show the supramolecular feature of the dyads concerning the photophysical properties (i.e. light harvesters show one major absorption band corresponding to one chromophore).33-36

The fluorescence of the compounds was also studied (Fig. 1). In order to compare the fluorescence of the dyads with that of the reference compounds, optically matched solutions (the solutions in comparison show the same absorbance at the excitation wavelength, thus the concentration of the solution varied slightly) were used (Fig. 1). For **FcB-1**, the fluorescence band is centered at 516 nm, similar to the fluorescence emission of the reference compound. However, the fluorescence intensity of **FcB-1** is much weaker than that of **B-1** (Fig. 1d). A similar quenching effect on the fluorescence of the reference compounds was observed for **B-2/FcB-2** and **B-3/FcB-3** (Fig. 1e and f), and the quenching effect in **FcB-2** is weaker than that in **FcB-1** and **FcB-3**.



Fig. 1 UV-Vis absorption of (a) **B-1** and **FcB-1**. (b) **B-2** and **FcB-2**. (c) **B-3** and **FcB-3**. The fluorescence emission spectra of (d) **B-1**, **FcB-1** ($\lambda_{ex} = 475$ nm, A = 0.194). (e) **B-2** and **FcB-2** ($\lambda_{ex} = 508$ nm, A = 0.291) and (f) **B-3**, **FcB-3** ($\lambda_{ex} = 482$ nm, A = 0.313). Optically matched solutions were used for the fluorescence emission studies. $c = 1.0 \times 10^{-5}$ M in DCM, 20 °C.

Based on the absorption spectra and the quenching effects, the PET mechanism is proposed to be responsible for the fluorescence quenching in the dyads.37 In the ground state, there is no significant electronic interaction between the Fc and the Bodipy moieties in the dyads (Fig. 1a-c). Conversely, emission quenching effects of FcB-1-FcB-3 happen upon irradiation, indicating that the PET process occurs in the excited state from the Fc moiety (strong electron donor) to the singlet excited state of Bodipy (electron acceptor fluorophore). The PET mechanism was also confirmed by the calculation of the Gibbs free energy changes (ΔG° , vide infra), and these results were in agreement with the experimental data reported previously.^{26,28,29} To the best of our knowledge, this is the first study of the fluorescence quenching of Bodipy by Fc based on the PET mechanism. It should be pointed out that fluorescence resonance energy transfer (FRET) is unlikely the guenching mechanism, because Fc does not show strong absorption in the emission region of the Bodipy moiety (note a large molar extinction coefficient of the energy acceptor is mandatory for efficient FRET).³⁸

The solvent polarity-dependence of the fluorescence of the dyads was studied and compared with the organic references (Fig. 2). The luminescence spectra of the optically matched solutions of **FcB-1** in different solvents are presented in Fig. 2a.

The fluorescence is weaker in acetonitrile than in less polar solvents, such as toluene. There is a slight blue-shift and intensity decreasing of the band maxima in passing from toluene to dichloromethane, then to acetonitrile. For the reference compound **B-1** (Fig. 2d), however, no such clear dependence was observed. This result indicated that the PET process happened in **FcB-1**. For **FcB-2**, the fluorescence intensity in dichloromethane is essentially identical to that in toluene, while it decreases obviously in acetonitrile. Similar solvent polarity-dependent fluorescence emission was observed for **B-2**. No strong polarity-dependent fluorescence was observed for **FcB-3** (Fig. 2c), as well as for the reference compound **B-3** (Fig. 2f).²⁴

The fluorescence decay of compounds **FcB-1**, **FcB-3** and the reference Bodipy compounds **B-1** and **B-3** was recorded at 512 nm upon excitation using a 445 nm picosecond laser (Table 1). For **B-1**, a single exponential decay trace was observed (Fig. 3a), which gives a fluorescence lifetime of 3.72 ns (Table 1). For the dyad **FcB-1**, however, a clear biexponential decay of the emission was observed, which contains a short fluorescence lifetime ($\tau_1 = 0.42$ ns, 85.2%) and a longer lifetime component ($\tau_2 = 4.29$ ns, 14.8%). The shorter lifetime can be attributed to the charge separation process (with which the fluorescence of the Bodipy chromophore was quenched), whereas the longer lifetime component is close to the intrinsic fluorescence lifetime of Bodipy (3.72 ns).

Previously a biexponential decay trace was observed for the Fc-PDI dyad, for which the quenching of the fluorescence of PDI was attributed to PET.³⁹ Similar results were observed for **B-3** (Fig. 3b). For **B-3**, the decay obeyed the single exponential function giving a single fluorescence lifetime ($\tau = 2.42$ ns). On the other hand, the decay of triad **FcB-3** consisted of a fast decay component ($\tau_1 = 0.64$ ns, 19%) and a slow component ($\tau_2 = 2.78$ ns, 81%). From the shorter lifetime compared with **B-3**, an appreciable increase in the decay rate of triad **FcB-3** was observed. The shorter τ_1 value (0.64 ns) of triad **FcB-3** can be attributed predominantly to charge separation between the Fc and Bodipy moieties, while the longer τ_2 value (2.78 ns) is similar to the intrinsic fluorescence lifetime of the **B-3** chromophore (2.42 ns).

Based on the fluorescence quenching in dyads and the intrinsic fluorescence lifetimes of the Bodipy parts in the dyads (from the reference compounds **B-1**, **B-2** and **B-3**), the electron transfer rate constants in the dyads were calculated using eqn (1).⁴⁰

$$k_{\rm ET} = \frac{1}{\tau_{\rm Dyads}} - \frac{1}{\tau_{\rm Ref}} \tag{1}$$



Fig. 2 The emission spectra of (a) FcB-1 (λ_{ex} = 474 nm A = 0.171), (b) FcB-2 (λ_{ex} = 508 nm, A = 0.307), (c) FcB-3 (λ_{ex} = 482 nm, A = 0.149) (d) B-1 (λ_{ex} = 475 nm, A = 0.209), (e) B-2 (λ_{ex} = 508 nm, A = 0.281) and (f) B-3 (λ_{ex} = 478 nm, A = 0.194) in toluene, CH₂Cl₂ and CH₃CN. Optically matched solutions were used c = ca 1.0 × 10⁻⁵ M (the concentrations were varied slightly to obtain optically matched solutions). 20 °C.

Table 1 Photophysical properties of FcB-1, FcB-2, FcB-3, B-1, B-2 and B-3^a

Comp.	$\lambda_{abs}{}^{b}/nm$	ε^{c}	$\lambda_{\rm em}{}^d$	τ^{e}/ns	$\tau_{\mathrm{T}}^{f}(\mu \mathrm{s})$	Φ_{Δ}	${\Phi}^{h}\left(\% ight)$	$k_{\mathrm{ET}}{}^{i}\left(\mathrm{s}^{-1} ight)$
FcB-1	504	7.78	514	0.42 (85.2%), 4.29 (14.8%)	j	<i>j</i>	8.3	$(2.11 \pm 0.11) imes 10^9$
FcB-2	538	8.02	551	0.18 (91.7%), 4.73 (8.3%)	j	<i>j</i>	4.9	$(1.39 \pm 0.07) \times 10^9$
FcB-3	505	6.34	518	0.64(19.0%), 2.78(81.0%)	j	<i>j</i>	0.08	$(1.15 \pm 0.06) \times 10^9$
B-1	504	9.18	514	3.72 (100%)	j	<i>j</i>	81	j
B-2	537	8.84	553	0.24 (100%)	83.96	0.74^{g}	7.8	<i>j</i>
B-3	506	7.05	518	2.42 (100%)	j	<i>j</i>	25.4	<i>j</i>

^{*a*} The excitation wavelengths for **B-1**, **B-3**, **FcB-1** and **FcB-3** were 480 nm, **B-2**, **FcB-2** were 515 nm $(1.0 \times 10^{-5} \text{ M}, 20 \text{ °C} \text{ in toluene})$. ^{*b*} Absorption wavelength. ^{*c*} Molar extinction coefficient, ε : $10^4 \text{ M}^{-1} \text{ cm}^{-1}$. ^{*d*} Fluorescence emission wavelength. ^{*e*} Fluorescence lifetimes in toluene. ^{*f*} Triplet state lifetimes. ^{*g*} Quantum yield of singlet oxygen (¹O₂), with 2,6-diiodo-Bodipy as the standard ($\Phi_{\Delta} = 0.79$ in CH₂Cl₂), $\lambda_{ex} = 526.5$ nm. ^{*h*} Fluorescence quantum yields in toluene, **B-1**, **B-3**, **FcB-1** and **FcB-3** with boron-dipyrromethene(Bodipy) (0.72 in THF) as the standard, **B-2** and **FcB-2** with 2,6-diiodo-Bodipy (0.027 in CH₃CN) as the standard. ^{*i*} The electron transfer rate constants in the dyads calculated using eqn (1). The error was estimated to be $\pm 5\%$. ^{*j*} Not applicable or not observed.



Fig. 3 Decay profiles of fluorescence lifetime measurement of (a) FcB-1 and B-1; (b) FcB-3 and B-3 (c = 1.0 \times 10⁻⁵ M) in DCM. 20 °C.

 τ_{Ref} is the lifetime of the reference compounds (**B-1** or **B-3**) and τ_{Dyads} is the lifetime of the dyads (**FcB-1** or **FcB-3**). The data are compiled in Table 1.

The electron transfer rate constant of the PET process in compound **FcB-3** is $(1.15 \pm 0.06) \times 10^9 \text{ s}^{-1}$, which is smaller than that in **FcB-1** $(2.11 \pm 0.11) \times 10^9 \text{ s}^{-1}$. This result indicates that the linker between the chromophores is crucial for the electron transfer. We also used a click reaction to connect the

Fc and the 2,6-diiodoBodipy parts together (a moderate linker) to study the quenching effect of Fc on the triplet excited state of organic chromophores (FcB-2) from electron and energy transfer respectively. The electron transfer rate constant of FcB-2 is $(1.39 \pm 0.07) \times 10^9 \text{ s}^{-1}$. The electron transfer rate constants of the dyads are in agreement with the fluorescence quenching studies (Fig. 2).

Electrochemical study (cyclic voltammetry) and Gibbs free energy changes of PET

The redox properties of the compounds were studied using cyclic voltammetry (Fig. 4). For **B-1**, a reversible oxidation wave at $E_{1/2} = +0.95$ V was observed. A reversible reduction wave at $E_{1/2} = -1.53$ V was observed. **B-2** and **B-3** show similar redox potentials (Fig. 4b and c). For the dyads **FcB-1**, **FcB-2** and **FcB-3**, similar redox potentials attributed to the Bodipy moiety were observed, indicating a weak electronic interaction between the Fc and the Bodipy moieties in the dyads. The redox potential of the Fc moiety overlaps with the free Fc added in the solution (except in the case of **FcB-3**). The 1,2,3-triazole moiety exhibited



Fig. 4 Cyclic voltammogram of (a) B-1, (b) B-2, (c) B-3, (d) FcB-1, (e) FcB-2, (f) FcB-3 ($c = 5.0 \times 10^{-4}$ M). For (a)–(e), $c = 1.0 \times 10^{-3}$ M. In deaerated CH₂Cl₂ solutions containing the compounds, 0.10 M Bu₄NPF₆ as the supporting electrode, Ag/AgNO₃ as the reference electrode, scan rate: 100 mV s⁻¹. For all compounds ferrocene (Fc) ($c = 1.0 \times 10^{-3}$ M) was used as the internal reference. 20 °C.

irreversible oxidation waves in the range of 0.3–0.6 V (*vs.* Ag/AgNO₃), this assignment was confirmed by **FcB-0** (see ESI,† Fig. S33).

In order to study the PET process of the dyads, the Gibbs free energy changes (ΔG_{CS}°) of the PET processes of the dyads were calculated according to the Weller equation (eqn (2) and (3)),³⁴ and the energy level of the charge separation energy states (E_{CS}) were calculated according to eqn (4).

$$\Delta G_{\rm CS}^{\circ} = e[E_{\rm OX} - E_{\rm RED}] - E_{0,0} + \Delta G_{\rm S}$$
(2)

$$\Delta G_{\rm S} = -\frac{e^2}{4\pi\varepsilon_{\rm S}\varepsilon_0 R_{\rm CC}} - \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{R_{\rm D}} + \frac{1}{R_{\rm A}}\right) \left(\frac{1}{\varepsilon_{\rm REF}} - \frac{1}{\varepsilon_{\rm S}}\right)$$
(3)

$$E_{\rm CS} = e[E_{\rm OX} - E_{\rm RED}] + \Delta G_{\rm S} \tag{4}$$

where $\Delta G_{\rm S}$ is the static Coulombic energy, which is described by eqn (2). e = electronic charge, E_{OX} = half-wave potential for oneelectron oxidation of the electron-donor unit, E_{RED} = half-wave potential for one-electron reduction of the electron-acceptor unit; note herein the anodic and cathodic peak potentials were used because in some cases the oxidation is irreversible. Potential $E_{1/2}$ cannot be derived, therefore the $E_{0,0}$ energy level was estimated from the crossing point of normalized absorption and emission spectra in CH₂Cl₂ (for the singlet excited state) (see ESI,† Fig. S34); $\varepsilon_{\rm S}$ = static dielectric constant of the solvent, $R_{\rm CC}$ = center-to-center separation distance between the electron donor (Fc unit) and the electron acceptor (Bodipy unit), determined by DFT optimization of the geometry R_{CC} $(FcB-1) = 16.6 \text{ Å}, R_{CC}(FcB-2) = 16.6 \text{ Å} and R_{CC}(FcB-3) = 12.8 \text{ Å}. R_{D}$ is the radius of the ferrocene part based electron donor, R_A is the radius of the electron acceptor, ε_{REF} is the static dielectric constant of the solvent used for the electrochemical studies, ε_0 is the permittivity of free space (8.85 \times 10⁻¹² m⁻³ kg⁻¹ s⁴ A²). The solvents used in the calculation of free energy of the electron transfer are toluene (ε_{s} = 2.4), CH₂Cl₂ (ε_{s} = 9.1), CH₃CN $(\varepsilon_{\rm S} = 37.5)$. 20 °C.

Based on these parameters, for FcB-2 in CH_2Cl_2 , ΔG_s is calculated to be -0.09 eV. For FcB-2, we assume that the singlet electron transfer from the electron donor to the electron acceptor is faster than any electron transfer, or charge separation. With the singlet excited state of the energy donor populated

Table 2 Electrochemical data for compound B-1, B-2, B-3, FcB-1, FcB-2 and FcB-3

(reference compound **B-2**), intersystem crossing (ISC) will occur. For compound **B-2**, ISC is much faster than the fluorescence process, therefore we postulate that ISC will occur before any electron transfer process. $E_{0,0}$ of compound **B-2** was approximated by the T₁ state energy level (1.52 eV).³³ With reference **B-2** as the electron acceptor, then $\Delta G_{CS}^{\circ} = 0.18 - (-1.30) - 1.52 - 0.09 = -0.15$ eV. Therefore the triplet excited state localized on the electron acceptor part (**B-2**) is likely to oxidize the energy donor Fc part.

If the electron transfer from the electron donor to the acceptor occurs at the singlet excited state of electron donor (reference unit **B-2**), then $E_{0,0}$ of compound **B-2** is approximated as 2.28 eV. With reference **B-2** as the electron acceptor, $\Delta G_{CS}^{\circ} = 0.18 - (-1.30) - 2.28 - 0.09 = -0.89$ eV. Based on these analyses, the intramolecular electron transfer in **FcB-2** is much significant from the electron donor (ferrocene part) to the electron acceptor (**B-2**) at the singlet excited state. Similarly the Gibbs free energy change of **FcB-1** and **FcB-3** was also calculated and the data are summarized in Table 2. It was found that the PET is exothermic for the dyads, and the Gibbs free energy change of the PET is more negative in polar solvents than in less polar solvents.

Switching of the fluorescence of the dyads by redox methods

Previously the ferrocene/ferrocenium (Fc/Fc⁺) pair transformation in the Fc–PDI dyad was used for switching of the fluorescence of the PDI moiety.³⁸ Herein the switching of the fluorescence of dyad **FcB-1** was achieved by an electrochemical method (Fig. 5, the fluorescence spectra were recorded using a spectroelectrochemical cuvette).

Upon oxidation of the Fc moiety (0.7 V was imposed, *vs.* Ag/AgNO₃) to Fc⁺, the fluorescence band at 517 nm was enhanced gradually, a maximum of 7.0-fold enhancement was observed (Fig. 5a). This fluorescence enhancement upon oxidation of Fc may be attributed to the cease of the PET with Fc as the electron donor because Fe³⁺ is unable to be oxidized further. Upon reduction, *i.e.* Fc⁺ \rightarrow Fc transformation (-0.3 V imposed on the working electrode, *vs.* Ag/AgNO₃), the fluorescence band at 517 nm was decreased (Fig. 5b). Similar results were observed for **FcB-3** (see ESI,[†] Fig. S35).

Compd	$E_{\rm ox}^{a}$ (V)	$E_{\mathrm{red}}^{a}(\mathbf{V})$	$\Delta G_{\rm S}$ (eV)			$\Delta G_{\rm CS}^{\circ}$ (eV)			$E_{\rm CS}$ (eV)		
			Toluene	$\mathrm{CH}_2\mathrm{Cl}_2$	CH_3CN	Toluene	$\mathrm{CH}_2\mathrm{Cl}_2$	CH_3CN	Toluene	$\mathrm{CH}_2\mathrm{Cl}_2$	CH ₃ CN
B-1	+0.95	-1.53	b	b	b	b	b	b	b	b	b
B-2	+1.08	-1.28	b	b	b	b	b	b	b	b	b
B-3	+0.97	-1.50	b	b	b	b	b	b	b	b	b
FcB-1	+0.19/+0.90	-1.53	+0.29	-0.09	-0.20	-0.42^{c}	-0.82^{c}	-0.92^{c}	+2.02	$+1.63^{c}$	$+1.52^{c}$
FcB-2	+0.18/+1.10	-1.30	+0.29	-0.09	-0.20	-0.49^{c}	-0.89^{c}	-0.99^{c}	+1.78	$+1.38^{c}$	$+1.28^{c}$
						$+0.25^{d}$	-0.15^{d}	-0.25^{d}	b	b	b
FcB-3	+0.32/+0.97	-1.50	+0.49	-0.12	-0.29	-0.12^{c}	-0.73^{c}	-0.90^{c}	+2.31	+1.69 ^c	$+1.53^{c}$

^{*a*} Recorded with $[Bu_4N][PF_6]$ as the electrolyte in CH₂Cl₂ (0.1 M) at room temperature with a scan rate of 100 mV s⁻¹. Potentials are expressed as the half-wave potentials ($E_{1/2}$) in volts *vs.* Ag/AgNO₃. For all compounds using ferrocene as an internal reference ($c = 1.0 \times 10^{-3}$ M). ^{*b*} Not determined. ^{*c*} $E_{0,0}$ of complexes was approximated by the energy levels of the excited states of ¹BDPY*. ^{*d*} $E_{0,0}$ of complexes was approximated by the energy levels of the excited states of ³BDPY*. 20 °C.

Fig. 5 (a) The fluorescence intensity changes of **FcB-1** ($\lambda_{ex} = 480$ nm), upon oxidation at 0.7 V *versus* Ag/AgNO₃ (from neutral state to oxidative state of Fc⁺). (b) The fluorescence intensity changes of **FcB-1** ($\lambda_{ex} = 480$ nm), upon reduction at -0.3 V *versus* Ag/AgNO₃ (from the oxidative state to the neutral state of Fc). Potentials were applied using an electrochemical workstation. The sample solutions contained the compound **FcB-1** (5.0×10^{-4} M) and 0.1 M [Bu₄N][PF₆] as the supporting electrolyte in CH₃CN, the fluorescence spectra were recorded upon excitation at 480 nm. The spectra were recorded *in situ* using a spectroelectrochemical cuvette. 20 °C.

The fluorescence of a PDI-Fc triad was modulated by the electrochemical approach of reversible oxidation/reduction of the Fc moiety.^{38,40} The electrochromism of the Fc–Bodipy conjugate (the two chromophores were connected by a π -conjugation linker) was studied, but the switching of the fluorescence of the dyad was not studied.⁴¹ However, no switching of the fluorescence of the Fc–Bodipy dyad *via* electrochemical reduction/oxidation has been reported.²⁴ The fluorescence intensity of **FcB-3** was increased by about 20-fold (see ESI,† Fig. S36).

The fluorescence intensity was recovered after each step and found to be rapidly and almost completely recovered upon completion of the step; thus, the reversibility of the switching process was proved. As a result, a fast and vigorous redox-fluorescence switch can be established with dyads **FcB-1** and **FcB-3** (Fig. 6), by taking advantage of the properties of the ferrocene electron donor and the Bodipy as a fluorescent read-out unit.⁴²

To verify the reversibility of the electrochemically controlled fluorescence switching, different scanning rates were used to check the complete electrochemical reversibility of the Fe^{II}/Fe^{III}



Fig. 6 Chronoamperometric analysis of (a) **FcB-1** ($c = 5.0 \times 10^{-4}$ M in CH₃CN), the potentials were switched at +0.7 V for 600 s (for oxidation) and then -0.3 V for 300 s (for reduction), the fluorescence intensity at 512 nm was monitored ($\lambda_{ex} = 480$ nm). (b) **FcB-3** ($c = 5.0 \times 10^{-4}$ M) the potentials were switched at +0.9 V for 440 s (for oxidation) and -0.2 V for 200 s (for reduction), the fluorescence intensity at 514 nm was monitored ($\lambda_{ex} = 480$ nm). 0.1 M [Bu₄N][PF₆] as the supporting electrolyte, the potentials are *versus* Ag/AgNO₃. 20 °C.



Fig. 7 Fluorescence spectra of (a) **FcB-1** ($c = 1.0 \times 10^{-5}$ M), (b) **FcB-3** ($c = 1.0 \times 10^{-5}$ M) in THF in the presence of different amounts of Fe(ClO₄)₃ ($\lambda_{ex} = 480$ nm). The inset shows the photographs of the emission changes in the solution with Fe(ClO₄)₃, $c = 1.5 \times 10^{-5}$ M in THF, 20 °C.

redox couple of the dyads (see ESI,† Fig. S36).⁴² These results show that the reversibility of the redox process is excellent. Thus our present study offers a new approach for controlling the fluorescence of Bodipy.

Chemical oxidation experiments were also performed to confirm that the fluorescence of the Bodipy moiety can be switched-ON with an oxidant. With increasing concentration of $Fe(ClO_4)_3$ in the solution, the fluorescence emission of **FcB-1** was enhanced (Fig. 7a), a distinct fluorescence switching ON effect was observed (inset of Fig. 7a). Similar results were observed for **FcB-3** (Fig. 7b).

In order to determine the evolution of the fluorescence intensity after the addition of one equivalent of $Fe(ClO_4)_3$, the fluorescence emission was recorded every minute. The fluorescence intensity enhancement is saturated after about 20 min for **FcB-1** and 15 min for **FcB-3** (see ESI,† Fig. S37 and S38), respectively. The effect of the oxidizing agent on the fluorescence intensity of **B-1** and **B-3** was not obvious (see ESI,† Fig. S39). More than 80% of the fluorescence intensity of Bodipy chromophores was recovered. This result is much higher than previously reported 33.2%.^{40,42–44} However, no suitable reductant was found to switch OFF the fluorescence of the Bodipy dyad, this situation is similar to a previous study on the switching of the fluorescence of Fc-PDI and Fc-porphyrin with $Fe(ClO_4)_3$.^{40,44}

The switching of the fluorescence of the Bodipy moiety in the dyads is summarized in Scheme 2 and Scheme S1 (ESI[†]). Upon photoexcitation of the Bodipy moiety, the singlet excited



Scheme 2 Mechanism of photoinduced electron-transfer quenching and off/on redox switching of fluorescence emission for the ferrocenebodipy dyad.

state in **FcB-1** was quenched by the PET process, thus the fluorescence was substantially reduced as compared with the emission of the Bodipy moiety. Upon oxidation of the Fc moiety in the dyad, the PET process is inhibited, as a result, the fluorescence of the Bodipy was recovered.

The effect of Fc on the triplet excited state of Bodipy

It is well known that long-lived triplet excited states are important for photocatalysis,^{1–3} photodynamic therapy (PDT),^{4–11} TTA upconversion^{8,33} and molecular devices.^{4,5} However, the quenching effect of Fc on the triplet excited state of Bodipy was rarely studied. 1,2,3-Triazole as the linker was selected to construct **FcB-2**. From electron and energy transfer, respectively, this kind of linker benefits further study of the quenching effect of Fc on the triplet excited state of organic chromophores (*e.g.* 2,6-diiodoBodipy). Triplet–triplet annihilation (TTA) upconversion, an important application of triplet photosensitizers,^{4,10,30,33} provides an indirect way to study the quenching effect of Fc on the triplet excited state. Herein, TTA upconversion with **FcB-2** as the triplet photosensitizer and perylene as the triplet acceptor was studied, and no TTA upconversion luminescence was observed (see ESI,† Fig. S40).

In order to study the reason for the lack of TTA upconversion with **FcB-2** as the triplet photosensitizer, we carried out two control experiments. **B-2** was used as the triplet photosensitizer and perylene as the triplet acceptor/emitter, and strong TTA upconversion was observed (Fig. 8a). With the addition of ferrocene into the mixture, however, the TTA upconversion intensity was reduced. Two processes may be responsible for this quenching effect, *i.e.* quenching of the fluorescence of perylene by Fc, or quenching of the triplet excited states (either the triplet excited state of **B-2** or the triplet state of perylene). Thus we studied the fluorescence variation of perylene in the presence of Fc (Fig. 8b). The results show that the fluorescence of perylene was hardly quenched by Fc. Therefore, we propose that Fc is a quencher for the triplet excited state.

The triplet excited states of **FcB-2** and the reference **B-2** in toluene were studied using nanosecond transient absorption spectroscopy (Fig. 9). Normal nanosecond transient absorption spectra were observed for **B-2**, which are in accordance with a previous report (Fig. 9a and inset).³⁰ For **FcB-2** in toluene, no transient signal was detected using our nanosecond transient



Fig. 8 (a) The upconverted perylene fluorescence and the residual fluorescence of **B-2** with increasing ferrocene concentration ($\lambda_{ex} = 532$ nm). *c* [**B-2**] = 1.0×10^{-5} M, *c* [perylene] = 4.0×10^{-5} M in deaerated toluene. (b) The fluorescence emission of perylene with increasing amounts of ferrocene. *c* [perylene] = 4.0×10^{-5} M in deaerated toluene, 20 °C.



Fig. 9 Comparison of the nanosecond transient absorption spectra of (a) **B-2** and (b) **FcB-2**; (c) decay trace of the transient of **B-2** and **FcB-2** at 525 nm. Excited with a 532 nm nanosecond pulsed laser. $c = 1.0 \times 10^{-5}$ M in deaerated toluene, 20 °C.

absorption spectrometer (time-resolution of 10 ns) (Fig. 9b and inset). A similar result was observed for **FcB-2** in acetonitrile (see ESI,† Fig. S41).

It should be pointed out that toluene is a non-polar solvent, and intramolecular electron transfer of **FcB-2** hardly occurs $(\Delta G_{\rm CS}^{\circ} > 0 \text{ eV})$ in toluene. Therefore, we propose that, in toluene (apolar solvent), triplet-triplet energy transfer (TTET) from the Bodipy moiety to Fc may be responsible for the quenching of the triplet excited state of the Bodipy moiety.⁴⁵ However, the triplet state of Fc shows a very weak excited state absorption (ESA) at 617 nm ($\varepsilon = 450 \text{ M}^{-1} \text{ cm}^{-1}$).²⁶ There is no significant transient signal in nanosecond transient absorption spectra assigned to the T₁ state of Fc,⁴⁶ thus we propose no Fc triplet state was produced.

Fortunately, the T_1 state energy level of Fc could be calculated using Stern–Volmer quenching constants (Fig. 10 and 11) and eqn (5).^{25,27,47} The triplet state lifetime of **B-2** was reduced gradually upon increasing the concentration of Fc (Fig. 11 and Table S1, ESI†). The Stern–Volmer quenching curve was plotted (Fig. 11). Given that the T_1 state of Bodipy was quenched by Fc through the TTET process, the energy transfer rate constants should be given by eqn (5).^{25,47}

$$k_{\rm q} = k_{\rm D} \cdot \frac{1}{1 + \exp(-\Delta E_{\rm T}/kT)} \tag{5}$$

where $k_{\rm D}$ is the diffusion-controlled rate constants, k is Boltzmann's constant and $\Delta E_{\rm T} = E_{\rm T}(\text{Donor}) - E_{\rm T}(\text{Acceptor})$.



Fig. 10 Quenching of the triplet state lifetime of **B-2** with increasing concentrations of ferrocene, (a) **B-2**, *c* [ferrocene] = $0 - 5.0 \times 10^{-5}$ M. In deaerated toluene. (b) **B-2**, *c* [ferrocene] = $0 - 5.0 \times 10^{-5}$ M. In deaerated CH₃CN. 25 °C.

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Fig. 11 Stern–Volmer plots for triplet state lifetime quenching of **B-2** with increasing concentrations of ferrocene, upon pulsed excitation (λ_{ex} = 515 nm). c [**B-2**] = 1.0 × 10⁻⁵ M in deaerated toluene and CH₃CN, 20 °C.

The Stern–Volmer quenching constant of **B-2**/Fc was calculated as $K_{\rm SV} = (5.09 \pm 0.14) \times 10^5 \text{ M}^{-1}$ in toluene. The bimolecular quenching constant $k_{\rm q}$ was calculated to be (6.06 ± 0.17) × $10^9 \text{ M}^{-1} \text{ s}^{-1}$ in toluene (Table S2, ESI†) according to eqn (6). τ_0 is the triplet state lifetime of the triplet energy donor.

$$k_{\rm q} = K_{\rm SV}/\tau_0 \tag{6}$$

The diffusion-controlled bimolecular quenching rating constants $k_{\rm D}$ can be calculated using the Smoluchowski equation (eqn (7)).

$$k_{\rm D} = 4\pi R N D / 1000 = \frac{4\pi N}{1000} (R_{\rm f} + R_{\rm q}) (D_{\rm f} + D_{\rm q})$$
(7)

D is the sum of the diffusion coefficients of the energy donor (D_f) and quencher (D_q) , *N* is Avogadro's number. *R* is the collision radius, the sum of the molecule radii of the energy donor (R_f) and the quencher (R_q) .

Diffusion coefficients can be obtained from the Stokes-Einstein equation (eqn (8)).

$$D = kT/6\pi\eta R \tag{8}$$

k is Boltzmann's constant, η is the solvent viscosity, *R* is the molecule radius. For the molecule the radius of the energy donor (**B-2**) is 4.34 Å and that of the quencher (Fc) is 1.75 Å. According to eqn (7) the diffusion coefficient of the energy donor (**B-2**) is 8.43×10^{-6} cm² s⁻¹ and that of the quencher (Fc) is 2.09×10^{-5} cm² s⁻¹ (in toluene at 20 °C). Thus $k_{\rm D}$ was calculated to be 1.35×10^{10} M⁻¹ s⁻¹.

The triplet energy transfer rate constant was calculated to be $(6.06 \pm 0.17) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table S2, ESI†). Assuming that the **B-2** triplet excited state is quenched by energy transfer from the **B-2** triplet excited state to that of Fc, the triplet level of Fc can be calculated using eqn (5). From the values $k_D = 1.35 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k_q = (6.06 \pm 0.17) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in toluene, $\Delta E_T = E_T(\text{B-2}) - E_T(\text{Fc}) = -5.17 \times 10^{-3}$ eV. Thus, the triplet state level of Fc is estimated to be 1.53 eV.^{25,27} The triplet state level of Fc is close to **B-2** and previous report.^{25,27} Thus the TTET mechanism is responsible for the quenching of the triplet excited state of **B-2** in toluene.

Interestingly, the quenching effect is more significant in polar solvents such as acetonitrile than in toluene (Fig. 10 and 11). It may be due to the lower energy level of the charge-separated state in a polar solvent. In CH_3CN , the energy of the charge

separated state is calculated to be 1.28 eV ($E_{CS} = +0.18 - (-1.30) - 0.20 = +1.28$ eV). The energy level of the charge separated state is much lower than that of the triplet excited state of **B**-2 and even Fc, indicating that intermolecular electron transfer may be responsible for the faster quenching effect of **FcB-2** in CH₃CN. Thus both PET and TTET are responsible for the quenching of the triplet excited state of **B**-2.

Conclusions

In summary, three different Bodipy–ferrocene (Fc) dyads with different linkers between the Bodipy and the Fc moieties were prepared. Reversible electrochemical switching of the fluorescence of the Bodipy fluorophore was realized with Bodipy– ferrocene (Fc) dyads. The quenching of the triplet excited state of Bodipy by Fc was also investigated. The photophysical properties of the dyads were studied using steady-state UV-vis absorption spectroscopy, luminescence, electrochemical characterization, time-resolved fluorescence and nanosecond transient absorption spectroscopies. Two quenching mechanisms, PET and triplet-triplet-energy transfer, are responsible for the intramolecular and intermolecular quenching of the triplet excited state of the photosensitizer.

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