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ARTICLE

An experimental and theoretical study of Dimethylaminostyryl BODIPY - Perylenetetracarboxylic derivatives dyads: synthesis, properties and DFT calculation.

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Dimethylaminostyryl BODIPY-Perylene tetracarboxylic derivatives (PTAC and PBI) dyads, **OMePTAC-BODIPY**, **PTAC-BODIPY** and **PBI-BODIPY**, were synthesized and investigated by spectral and DFT methods. UV-Vis absorption spectra revealed that the absorption coefficients in the region from 350 nm to 600 nm were distinctly enhanced by incorporation perylene tetracarboxylic derivatives into BODIPY block. Due to photo-induced electron transfer effect, the fluorescence of the dyads were strongly quenched. Differential pulse voltammograms (DPV) were involved to evaluate the energy levels of the dyads. The oxidation peaks are almost exactly the same located at 0.53 eV vs Ag/AgCl, and the reduction peaks occurred at -1.1 eV, -1.0 eV and -0.5 eV, shifted toward positive potential values, for **OMePTAC-BODIPY**, **PTAC-BODIPY** and **PBI-BODIPY** respectively, indicating that the LUMO levels of dimethylaminostyryl BODIPY-Perylene tetracarboxylic derivatives dyads are precisely designed by varying acceptor units from BODIPYs meso-position. Singlet oxygen (¹O₂) experiments uncovered that ¹O₂ are much impeded along the increase of the electron affinity of electron acceptor units. the rates for the charge separation (*k_{CS}*) and charge recombination (*k_{CR}*) were deduced by the Marcus equation, for **OMePTAC-BODIPY** and **PTAC-BODIPY**, the *k_{CS}* (10¹¹ s⁻¹) are approximately three orders of magnitude faster than *k_{CR}* (10⁸ s⁻¹), which will be beneficial to the photoelectric conversion and energy storage process.

Introduction

Dipyrromethene boron difluorides (BODIPYs) are one of the most distinguished dyes for high absorbance, strong fluorescence emission and high photo-stability.¹ They are widely used in fluorescence imaging, light-to-electricity conversion, photodynamic therapy, sensors and so on.² However, considering the narrow absorption band, commonly from 470 nm to 550 nm, it is not entirely suitable for application in the fields of energy conversion/storage

processes or infrared therapy.³ Therefore, the explorations towards BODIPYs with a broader absorption region and high coefficient are very desirable.

Fortunately, BODIPYs can be synthesized and modified efficiently to prepare new materials containing rational structures and optimized energy levels. According to the previous reports, various methods were effectively used to embellish the aromatic cores, including functionalization at the α or β positions,⁴ increasing the π conjugation along backbone direction from 2/6 position,⁵ fusing aromatic rings to the pyrrole units,⁶ and introduction new groups to the meso-position of the BODIPY cores.⁷

Since the lowest unoccupied molecular orbital (LUMO) levels express less influenced while highest occupied molecular

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orbital (HOMO) levels are more sensitive to meso substituents,⁸ modification at the meso-position is a highly interesting area of study as more and more researchers put their eyes on this sphere. According to this principle, new materials with fixed LUMO levels and changed HOMOs could be designed exactly, thus allowing for the accurate synthesis of compounds with exact energy levels which are needed in special applications. There are two steps in our approach: i) modification or functionalization at the other locations on BODIPYs except the meso-position to form molecules with a particular HOMO level, ii) after the HOMO levels are fixed, diverse groups or building blocks can be introduced into the meso-position of BODIPYs to modulate the LUMO levels. Therefore, the BODIPYs possessing unique HOMO/LUMO levels will be efficiently synthesized.

Undoubtedly, incorporating donor and acceptor substituents in molecules is a vigorous strategy to regulate energy levels by donor-acceptor (D-A) effects.⁹ In recent years, perylene tetracarboxylic derivatives, including perylene bisimides (PBIs) and perylene tetracarboxylic tetraesters (PTACs), have strong appeals to scientists because of the potential to be used in a variety of applications, such as light emitting diodes (OLEDs), field effect transistors (OFETs), non-fullerene acceptors, etc.¹⁰

Brining BODIPYs and perylene tetracarboxylic derivatives together by conjugated effect is hopeful to promote intramolecular electron transfer, broaden the spectral absorption and change the properties eventually. However, though great progress has been made in PBIs based non-fullerene solar cells,¹¹ the photoelectric conversion efficiency (PCE) in solar cells with PTACs acting as electron acceptors are

very low at present.¹² Hence, the continued investigation of the differences between PBIs and PTAC, for example, the charge separation rates (k_{CS}) and charge recombination rates (k_{CR}) which are key factors in device testing, is a highly important endeavour.

In this paper, three meso-derivatized dimethylaminostyryl BODIPY dyes, **OMePTAC-BODIPY**, **PTAC-BODIPY** and **PBI-BODIPY** were synthesized with the principle of D-A interaction. The singlet oxygen (1O_2) production experiment was carried out to analyze the production of triplet species of these dyes after excitation. The acceptor influence to absorption and energy levels as well as Gibbs free energy of electron transfer were investigated both by spectroscopic methods and DFT calculations. In addition, the charge separation (CS) and charge recombination (CR) rates were calculated by Marcus equation. The difference of 1000 times between charge separation rates and charge recombination rates of PTACs based dyes imply that the PTACs dyes have are very promising for potential applications in solar energy storage fields, though the device measurements have not given benign results at present.

Experimental section

Instrumentation and method

1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer. Mass spectra (Q-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer. UV-vis spectra were measured with Hitachi (Model U-4010) UV-vis spectrophotometer in a 1cm quartz cell. Fluorescence emission spectra were measured with Hitachi fluorescence

spectrophotometer (F-4600). Phosphorescence spectra were investigated by Edinburgh luminescence spectrometer (FLS980). Differential pulse voltammetry (DPV) and cyclic voltammograms (CV) were recorded on a Zahner IM6e electrochemical workstation at a scan rate of 50 mV s⁻¹, with using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode, and ferrocene/ferrocenium as an external potential marker for the calibration of potential. 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) dissolved in DCM (HPLC grade) was employed as the supporting electrolyte.

In the present calculations, the B3LYP/6-31G(d) is used in the geometric optimizations, and the orbital energies are further corrected by the B3LYP/6-311G(d,p). All the calculations were performed with the Gaussian 09 software package.¹³ Since the absorption spectra were measured in DCM matrix, all the calculations were determined in a solvent environment with use of a polarizable continuum model (PCM), and the static dielectric constant of DCM ($\epsilon = 8.93$) was used. Based on these states, one can easily obtain the driven force (ΔG), reorganization energy (λ) and electronic coupling constant (V) allowing for the electron transfer rate to be calculated utilizing the Marcus equation.¹⁴

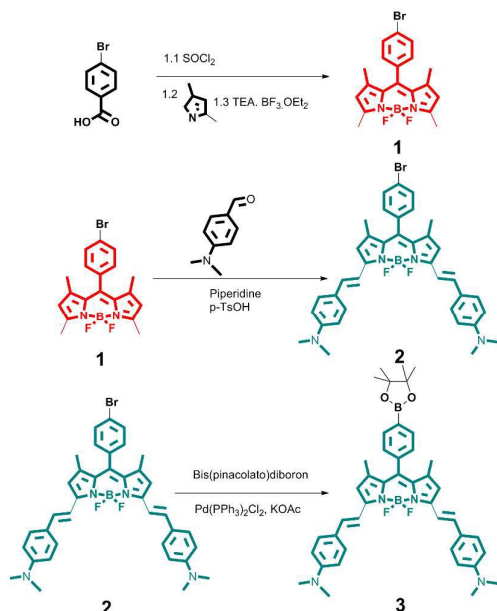
$$k = \frac{|V|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\lambda + \Delta G)^2}{4\lambda k_B T}\right)$$

where V is the electronic coupling between the excited states (for example, D^+A and D^+A^*), k_B is Boltzmann constant and T is temperature (in our calculation $T=298K$). To predict the rate,

one has to know λ , ΔG , and V . The ΔG is commonly estimated from the Rehm–Weller equation,¹⁵

$$\Delta G = E(D^+ / D) - E(A / A^-) - \Delta E_{00} - \frac{1}{4\pi\epsilon_r\epsilon_0} \sum_{i \in D^+} \sum_{j \in A^-} \frac{q_i q_j}{r_{ij}}$$

where $E(D^+/D)$, $E(A/A^-)$, and E_{00} correspond to the adiabatic ionization potential of the isolated donor, the adiabatic electronic affinity of the isolated acceptor, and the adiabatic energy difference of the D^+A and DA states, respectively, and the last term represents the Coulomb interaction. The reorganization energy is normally decomposed into internal (vibrational reorganization energy λ_{in}) and external (solvent λ_{out}) contributions. The four-point technique and two-sphere model were employed to calculate the λ_{in} and λ_{out} , respectively, the details of these techniques can be seen in anywhere.¹⁶ Since the present systems of the exciton and CT states are well represented by the single molecular orbital, the reduced two-state model (RTM) is suitable for the calculation of electronic couplings. With use of the obtained driving force, reorganization energy and coupling, the charge separation and charge recombination rates can be readily calculated by the Marcus equation.



Scheme 1. Synthesis route of dimethylaminostyryl BODIPYs

Materials

All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise specified. 8-(4-bromophenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **1** and bromination derivatives of PTAC or PBI, **4**, **5**, and **6** were prepared and characterized according to the literature reported previously.¹⁷ 4-phenyl substituted bodipy at meto position (compound **7**, see supporting information) was also synthesized.¹⁸

Synthesis of 8-(4-bromophenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (**1**)

Sealed with a balloon, 4-bromobenzoic acid (5.0 g, 25 mmol) was reacted with SOCl_2 (12.5 mL) at 80°C for 3h. Then, the excess SOCl_2 was removed under vacuum to prepare 4-bromobenzoyl chloride. After that, 50 mL of dry DCM was added to dissolve the residual, then 2,4-dimethylpyrrole (4.6 g, 48 mmol) in 20 mL of dry DCM was added slowly to the DCM solution of benzoyl chloride at room temperature and the

solution was stirred for about 20h when there was no pyrrole remaining. To the solution was added 10 mL of triethylamine followed 15 minutes later by the addition of $\text{BF}_3 \cdot \text{OEt}_2$ (10 mL, 81 mmol) and stirring continued for an additional 2h. The reaction mixture was washed with water thoroughly. The aqueous solution was extracted with DCM, organic layers were dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography using ethanol/DCM to afford **1** as a red solid (2.4 g, 25%). ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 5.99 (s, 2H), 2.55 (s, 6H), 1.41 (s, 6H).

Synthesis of brominated BODIPY (**2**)

8-(4-bromophenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **1** (670.0 mg, 1.7 mmol), 15 mg of $p\text{-TsOH} \cdot \text{H}_2\text{O}$, 4-dimethylaminobenzaldehyde (543.0 mg, 3.6 mmol), and 0.50 g of 4A molecular sieve were added to a 50 mL bottle. The bottle was then degassed and refilled with N_2 three times followed by the addition of 30 mL of toluene and 0.75 mL of piperidine, and this mixture was refluxed for 70h. The mixture was washed with water for several times to remove the sulfonic acid, the organic phase was evaporated, and after column chromatography on silica gel eluting with a gradient of DCM-petroleum ether (v/v 3:7) to DCM, **2** was obtained as a deep-green solid (605.0 mg, 25%). ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.3 Hz, 6H), 7.23 (d, J = 8.2 Hz, 4H), 6.71 (d, J = 8.3 Hz, 4H), 6.60 (s, 2H), 3.03 (s, 12H), 1.46 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.16, 150.98, 140.61, 136.68, 134.78, 132.79, 132.17, 130.78, 129.16, 125.17, 122.97, 117.48, 114.97, 112.17, 40.28, 29.71, 14.88. HRMS (EI), M/Z : calcd for $[\text{M}]^+$, 664.2184; found, 664.2213.

Synthesis of BODIPY boronic ester (**3**)

Under N₂ atmosphere, a 100 mL bottle was charged with a mixture of **2** (400.0 mg, 0.60 mmol), Pd(PPh₃)₂Cl₂ (130.0 mg, 0.18 mmol), bis(pinacolato)diboron (760.0 mg, 3.0 mmol), KOAc (588.0 mg, 6.0 mmol) and 40 mL of toluene. The mixture was refluxed overnight. After cooling to room temperature, 50 mL of water was added, and the biphasic system was filtered through a pad of Celite. The organic phase was separated and the aqueous solution was extracted with DCM, then the combined organic solution was concentrated under reduced pressure to give a green powder. The crude powder was immersion-cleaned by 120 mL of hexane for 1h and after filtration, the boronic ester of BODIPY **3** was obtained (421.0 mg, 99%). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 7.5 Hz, 2H), 7.55 (m, 6H), 7.35 (d, J = 7.5 Hz, 2H), 7.18 (m, 2H), 6.72 (d, J = 8.5 Hz, 4H), 6.59 (s, 2H), 3.03 (s, 12H), 1.40 (d, J = 7.2 Hz, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 152.90, 150.90, 141.00, 138.64, 136.32, 135.14, 132.80, 129.08, 128.27, 125.26, 117.23, 115.12, 112.17, 84.09, 40.28, 24.98, 14.76. HRMS (EI), M/Z: calcd for [M]⁺, 712.3931; found, 712.3941.

Synthesis of 1-bromo-7-methoxy-3,4,9,10-tetra(n-butoxy-carbonyl)-perylene(4)

K₂CO₃ (690.0 mg, 5.0 mmol), 1,7-dibromo-3,4,9,10-tetra(n-butoxy-carbonyl)-perylene(810.0 mg, 1.0 mmol), and 0.2 mL of CH₃OH were reacted in 30 mL of DMF for 24h at 80°C. After cooling to room temperature, 30 mL of water was added and extracted with 100 mL of DCM. The organic phase was washed with water 3 times, dried over Na₂SO₄, and the organic phase was evaporated. After column chromatography on silica gel eluting with a gradient of DCM-petroleum ether (v/v 1:1) to DCM, 410 mg of raw material was recycled as the first band and the second band was collected to afford **4** as a yellow solid (292.0 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ 8.98 (d, J = 7.9

Hz, 1H), 8.93 (d, J = 8.1 Hz, 1H), 8.29 (s, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 4.33 (m, 8H), 4.15 (s, 3H), 1.85 – 1.70 (m, 8H), 1.48 (d, J = 6.9 Hz, 8H), 0.98 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 168.43, 168.29, 168.09, 167.39, 155.33, 136.51, 132.78, 132.08, 131.99, 131.71, 131.16, 130.30, 130.01, 129.88, 128.66, 127.80, 127.04, 126.80, 122.84, 118.37, 117.68, 117.63, 65.62, 65.60, 65.40, 65.29, 56.66, 30.71, 30.65, 30.62, 19.30, 19.27, 13.80.

Synthesis of 1-bromo-3,4,9,10-tetra(n-butoxy-carbonyl)-perylene(5)

3,4,9,10-tetra(n-butoxy-carbonyl)-perylene(3.0 g, 4.6 mmol), K₂CO₃ (3.0 g, 22 mmol), 50 mL of DCM and 3 mL of Br₂ was stirred at room temperature for 1.5h. The excess bromine was removed by adding aqueous Na₂SO₃. Then, the crude product was purified through column chromatography on silica gel eluting with DCM. The second band was collected to yield 1-bromo-3,4,9,10-tetra(n-butoxy-carbonyl)-perylene as a brown solid (0.85 g, 25%). ¹H NMR (400 MHz, CDCl₃) δ 9.16 (d, J = 8.0 Hz, 1H), 8.32 (s, 1H), 8.25 (dd, J = 8.0, 2.4 Hz, 2H), 8.15 – 8.05 (m, 3H), 4.39 – 4.26 (m, 8H), 1.79 (m, 8H), 1.49 (m, 8H), 0.99 (m, 12H).

Synthesis of 1-bromo-N,N-bis-(ethylpropyl) perylene bisimide (6)

N,N-bis(ethylpropyl)perylene-3,4:9,10-tetracarboxylic bisimide (700.0 mg, 1.3 mmol), Br₂ (3.4 mL, 68.6 mmol), K₂CO₃ (700.0 mg, 5.1 mmol) and 15 mL of CHCl₃ were added to a 100 mL flask, the mixture were refluxed for 4h. The organic was washed with saturated Na₂SO₃ aqueous solution to remove excess Br₂ and the organic phase was separated and concentrated. After column chromatography on silica eluting with DCM-petroleum ether, 1-bromo-N,N-bis-(ethylpropyl) perylene bisimide **6** was obtained as a red solid in the second band (350.0 mg, 44%). ¹H NMR (400 MHz, CDCl₃) δ 9.81 (d, J =

8.2 Hz, 1H), 8.93 (s, 1H), 8.70 (d, J = 8.2 Hz, 3H), 8.63 (d, J = 8.0 Hz, 2H), 5.17 – 4.99 (m, 2H), 2.26 (m, 4H), 2.02 – 1.87 (m, 4H), 0.92 (m, 12H).

Synthesis of OMePTAC–BODIPY

Under N_2 , a 25 mL three-neck flask was charged with a mixture of **4** (125.0 mg, 0.17 mmol), boronic ester of BODIPY **3** (129.0 mg, 0.18 mmol), $Pd(PPh_3)_4$ (19.0 mg, 0.016 mmol), Na_2CO_3 (532.3 mg, 0.49 mmol), 10 mL of dry THF, and 1 mL of water. The solution was refluxed for 24 h. After cooling to room temperature, 10 mL of water was added and extracted with 60 mL of DCM 3 times, dried over Na_2SO_4 , and the organic phase was evaporated. After column chromatography on silica gel eluting with a gradient of DCM-petroleum ether (v/v 1:1) to DCM, and lastly with DCM-triethylamine (v/v 100:1) followed by recrystallization in DCM-ethanol, OMePTAC–BODIPY was obtained as a green powder (76.0 mg, 37%). 1H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, J = 7.9 Hz, 1H), 8.17 – 8.07 (m, 2H), 7.93 (s, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.57 (m, 8H), 7.41 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 7.4 Hz, 1H), 7.21 (m, 2H), 6.73 (d, J = 8.1 Hz, 4H), 6.64 (s, 2H), 4.46 – 4.24 (m, 8H), 4.19 (s, 3H), 3.04 (s, 12H), 1.83 – 1.73 (m, 8H), 1.55 – 1.41 (m, 14H), 1.10 – 0.90 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.61, 168.40, 168.13, 155.52, 144.07, 137.50, 134.16, 132.18, 131.59, 130.43, 130.28, 130.09, 129.41, 129.34, 129.15, 128.77, 126.86, 126.70, 123.28, 119.30, 118.07, 112.24, 67.93, 65.63, 65.46, 65.25, 56.77, 40.30, 30.76, 30.73, 30.64, 19.31, 19.28, 13.87, 13.80. HRMS (EI), M/Z : calcd for $[M]^+$, 1266.6065; found, 1266.6042.

Synthesis of PTAC–BODIPY

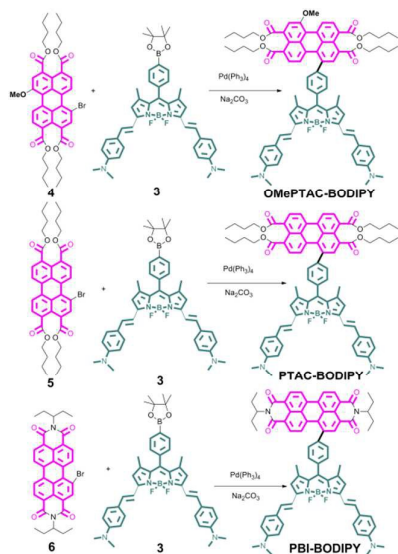
Under N_2 , a 25 mL three-neck flask was charged with a mixture of compound **5** (73.0 mg, 0.10 mmol), boronic acid ester of BODIPY **3** (81.9 mg, 0.12 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol), 5 mL of dry THF, and 0.5

mL of water. The mixture was stirred at 75°C overnight. After cooling to room temperature, 5 mL of water was added and extracted with 30 mL of DCM 3 times, dried over Na_2SO_4 , and the organic phase was evaporated. After column chromatography on silica gel eluting with a gradient of DCM-petroleum ether (v/v 1:1) to DCM and finally with DCM-triethylamine (v/v 100:1), followed by recrystallization in DCM-ethanol, PTAC–BODIPY was obtained as a green powder (59.0 mg, 48%). 1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 5.5 Hz, 2H), 8.12 (m, 3H), 7.80 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 7.8 Hz, 3H), 7.56 (d, J = 8.2 Hz, 5H), 7.49 – 7.42 (m, 3H), 7.22 (d, 2H), 6.73 (d, J = 8.4 Hz, 4H), 6.65 (s, 2H), 4.34 (m, 8.1 Hz, 8H), 3.04 (s, 12H), 1.83 – 1.73 (m, 8H), 1.50 (m, 14H), 1.00 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.28, 150.98, 138.50, 136.59, 135.40, 133.15, 131.48, 130.69, 130.31, 129.84, 129.17, 128.81, 125.23, 122.41, 117.46, 115.08, 112.19, 65.45, 65.33, 40.29, 30.69, 19.28, 13.80. HRMS (EI), M/Z : calcd for $[M]^+$, 1236.5959; found, 1236.5920.

Synthesis of PBI–BODIPY

Under N_2 atmosphere, a 25 mL three-neck flask was charged with a mixture of mono-bromo-PBI **6** (60.8 mg, 0.10 mmol), boronic acid ester of BODIPY **3** (78.3 mg, 0.11 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol), 5 mL of dry THF, and 0.5 mL of water. The mixture was stirred overnight at 75°C. After cooling to room temperature, 5 mL of water was added and extracted with 30 mL of DCM 3 times, and dried over Na_2SO_4 . The organic phase was evaporated and after column chromatography on silica gel eluting with a gradient of DCM-petroleum ether (v/v 1:1) to DCM followed by recrystallization in DCM-ethanol, PBI–BODIPY was obtained as a black powder (48.0 mg, 43%). 1H NMR (400 MHz, $CDCl_3$) δ 8.69 (m, 4H), 8.59 (s, 1H), 8.14 (d, J = 8.2 Hz, 1H), 8.05 (d, J =

8.1 Hz, 1H), 7.68 (d, $J = 7.9$ Hz, 2H), 7.56 (m, 8H), 7.21 (m, 2H), 6.69 (m, 6H), 5.07 (m, 2H), 3.04 (s, 12H), 2.27 (m, 4H), 2.05 – 1.86 (m, 7H), 1.52 (s, 3H), 1.02 – 0.84 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.99, 143.73, 140.88, 136.79, 136.30, 134.41, 132.71, 131.26, 130.23, 129.29, 129.21, 125.17, 123.70, 122.92, 117.68, 114.99, 112.17, 100.02, 57.89, 57.76, 40.28, 25.12, 25.07, 11.37. HRMS (EI), M/Z : calcd for $[\text{M}]^+$, 1114.5128; found, 1114.5125.



Scheme 2. Synthesis route of BODIPY- perylene tetracarboxylic dyads.

Results and discussion

Under the catalysis of piperidine and *p*-toluenesulfonic acid, compound **2** was obtained via Knoevenagel condensation from **1** and *p*-dimethylaminobenzaldehyde. **2** was transformed to boronic ester **3** under Miyaura borylation conditions. It is worth mentioning that either washing off traces of sulfonic acid after the condensation procedure or increasing palladium dosage will facilitate the borylation reaction. Otherwise, the substrates will not react completely. After immersion clean with hexane or recrystallization in hexane-DCM, the boronic ester **3** can be obtained cleanly. Subsequently, three meso-

derivatized BODIPYs were synthesized via Suzuki coupling from **3** and bromination derivatives of **PTAC** or **PBI**. The three D-A dyads, **OMePTAC-BODIPY**, **PTAC-BODIPY** and **PBI-BODIPY** manifest high solubility in DCM, chloroform, toluene, and tetrahydrofuran, while being less soluble in acetonitrile and alcohols. Their structures were identified by NMR and high resolution mass spectrometry unambiguously.

The UV-Vis absorption spectra of three new compounds in DCM are demonstrated in Figure 1(a). All these dyads exhibit well-defined vibronic π - π^* absorption bands with similar features: the absorption from 380 nm to 550 nm belongs to PBI or PTAC, while the stronger absorption from 570 nm to the near infrared region is assigned to dimethylaminostyryl BODIPY units,¹⁹ the maximum absorption is located at 705 nm with absorption coefficients up to $96500 \text{ M}^{-1}\text{cm}^{-1}$. The λ_{onset} values are 760 nm for both compound **2** and the three dyads, implying the same optical band-gaps about 1.63 eV. The abnormal phenomenon with no remarkable red-shift spectra in D-A molecules probably originate from the nonplanar configuration of the dyads.²⁰ Taking PBI-BODIPY as an example, the central phenyl unit at the meso-position are almost perpendicular to BODIPY plane with a dihedral angle of 90.03° and twisted around 128.01° with respect to the PBI plane (Figure 2). In the short wavelength region (380–550 nm), the absorption of three dyads are clearly enhanced than that of **2**, moreover, the absorption of PBI-BODIPY expresses red shifted about 40nm than that of PTAC-linked dyads, which are in accordance with the characteristics of perylene tetracarboxylic derivatives. When reacted with ceric ammonium nitrate ($1.0 \times 10^{-3} \text{ mol/L}$ in acetonitrile), new peaks located at 943 nm were found in the UV-vis spectra of compounds **2** and three dyads (Figure S1), which were assigned to the absorption of BODIPY cations.

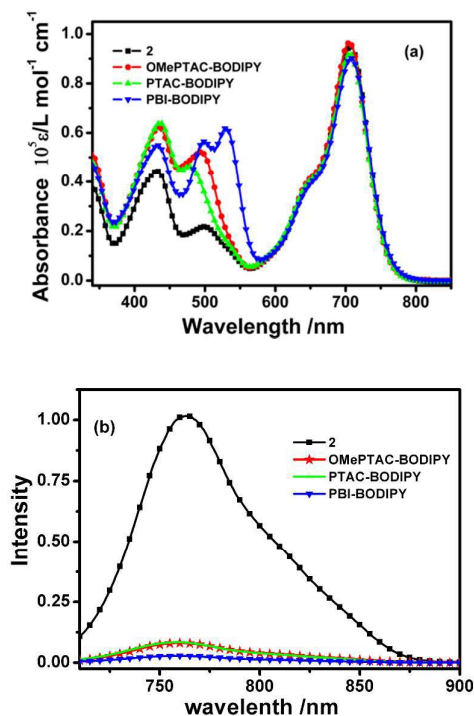


Figure 1. (a) UV-Vis absorption spectra of compounds **2** (black), OMePTAC-BODIPY (red) PTAC-BODIPY (green), and PBI-BODIPY (blue), at room temperature (1.0×10^{-5} mol/L). (b) Fluorescence emission spectra in DCM (1.0×10^{-5} mol/L), excited at 650 nm.

Figure 1(b) is the emission spectra in DCM solution ($\lambda_{\text{ex}} = 650$ nm, $\lambda_{\text{em}} = 760$ nm), compared with the highest emission intensity of the compound **2**, the fluorescence of dyads is substantially quenched. **PBI-BODIPY** has the much lower emission intensity than that of PTAC based BODIPYs. For there is no distinct overlap between the absorption of acceptor and the emission of donors, fluorescence resonance energy transfer process (FRET) can be ruled out, the fluorescence quenching should be attributed to photo-induced electron transfer (PET) mechanism.²¹ Near infrared phosphorescence spectra of compounds **7** and three dyads were carried out to investigate the triplet species (Figure S2), however, there were no obvious peaks in the near infrared region, which were most likely due to the low intersystem crossing efficiency (ISC) of BODIPYs.²²

For a better understanding of the electrochemical properties of the D-A dyes, as can be seen in Figure 2 and Figure 3, the frontier molecule orbital plots and the HOMO and LUMO levels were obtained by the single-point calculations at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level of theory.

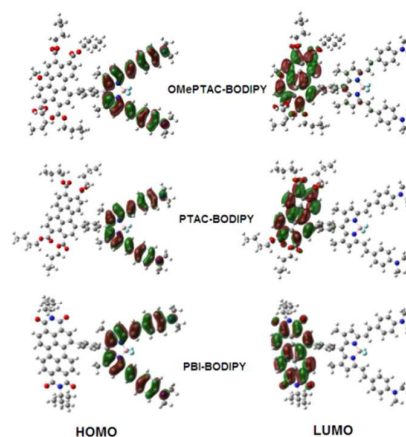


Figure 2. Frontier molecule orbital plots of OMePTAC-BODIPY, PTAC-BODIPY and PBI-BODIPY.

Differential pulse voltammograms (DPV) was used to evaluate the electrochemical properties of these dyads in DCM (Figure S4). The oxidation peaks are almost exactly the same located at 0.53 eV vs Ag/AgCl, implying the equivalence of the HOMO levels of these dyads. The result is perfect consistency with the conclusion of calculation,^{8b} that is, HOMO levels of BODIPYs are subtly influenced by meso-modification. The reduction reaction occurred at -1.1 eV, -1.0 eV, and -0.5 eV, shifted toward positive potential values, for OMePTAC-BODIPY, PTAC-BODIPY and PBI-BODIPY respectively. This indicates that the LUMO levels of dimethylaminostyryl BODIPY-perylene tetracarboxylic derivatives dyads are precisely designed by embedding different acceptor units in BODIPYs at the meso-position. The energy levels obtained by DPV and DFT method are listed in Figure 3. The ΔE_{calc} values are larger than the

ΔE_{redox} values by 0.5 eV, probably due to the calculations being performed under the implicit solvent conditions.

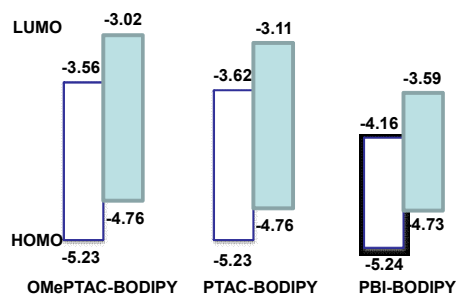


Figure 3. HOMO/LUMO levels of dyads, the red groups were obtained from DPV experiments, the blue groups were calculated by DFT methods.

According to the Rehm-Weller equation, the free energy changes in photoinduced intramolecular electron transfer process can be determined. The first excited state energy, E_{00} , is 1.63 eV for the dyads, deduced from fluorescence emission wavelength. The static Coulombic energy is -0.14 eV in DCM based on the DFT calculation. Hence, the free energy changes (ΔG_{CS}) are -0.10 eV, -0.16 eV, and -0.69 eV respectively for **OMePTAC-BODIPY**, **PTAC-BODIPY** and **PBI-BODIPY**, indicating thermodynamic permission for the formation of charge separated states, D^+A^- , via the singlet excited state of BODIPY.

The charge separated state energies (E_{CS}) are calculated following the corresponding equation (see Supporting Information),²³ which are 1.53 eV for **OMePTAC-BODIPY**, 1.47 eV for **PTAC-BODIPY**, and 0.94 eV for **PBI-BODIPY**.

Since the triplet state T_1 of $^3\text{BODIPY}^*$ is located at 1.10 eV (calculated by DFT in DCM), higher than E_{CS} of **PBI-BODIPY**, the triplet state of PBI-BODIPY will be quenched thoroughly. On the other hand, **PTAC-BODIPY** and **OMePTAC-BODIPY** possess high charge separated states, hence, $^3\text{BODIPY}^*$ of **PTAC-BODIPY** and **OMePTAC-BODIPY** may be produced after

excitation by light. To validate the speculation and fully elaborate the difference in electron transfer process triggered by acceptor changing, 1,3-diphenylisobenzofuran (DPBF) was employed as scavenger to switching photosensitive ability for singlet oxygen $^1\text{O}_2$. Because $^1\text{O}_2$ will destroy DPBF immediately, the characteristic absorption at 414 nm was used to detect singlet oxygen vicariously.²⁴

For **PBI-BODIPY**, the consumption rate is exceedingly similar with DPBF itself, implying no $^1\text{O}_2$ production. However, when mixed with perylene ester based dyads and irradiated by red laser at 650 nm, the absorbance of DPBF at 414 nm was quickly decreased. The linear slopes are -0.00805 and -0.00754 for **OMePTAC-BODIPY** and **PTAC-BODIPY** respectively, indicating that $^1\text{O}_2$ was generated. Using methylene blue as standard (0.57 in DCM), the quantum yield of singlet oxygen of **BODIPY 7**, **OMePTAC-BODIPY**, and **PTAC-BODIPY** were 12%, 3% and 2% respectively. In these cases, $^1\text{O}_2$ are much impeded along the increase of electron affinity of electron acceptor. Interestingly, **Br-BODIPY (2)** has a quantum yield of $^1\text{O}_2$ of about 4%, much lower than that of **BODIPY** itself, which does not express heavy atoms effect only but also it serves as an electron acceptor here primarily.²⁵

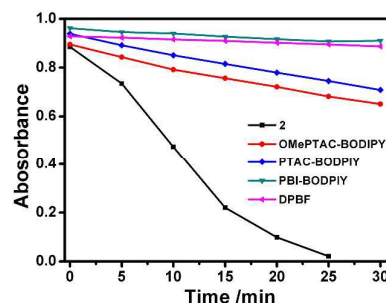


Figure 4. Switching of the singlet oxygen ($^1\text{O}_2$) photosensitizing ability. The decrease of the absorbance at 414 nm of DPBF as a function of irradiation time for OMePTAC-BODIPY, PTAC-BODIPY, PBI-BODIPY, and methylene blue ($\lambda_{\text{ex}} = 650$ nm). (The

concentration of DPBF was 4×10^{-5} mol/L, and the concentration of dyes is 1×10^{-6} mol/L in DCM), the experiment was carried out in the dark.

	CS					CR				
	$\Delta G_{CS}(eV)$	$\lambda_{in}(eV)$	$\lambda_{out}(eV)$	$\lambda(eV)$	$k(s^{-1})$	$\Delta G_{CR}(eV)$	$\lambda_{in}(eV)$	$\lambda_{out}(eV)$	$\lambda(eV)$	$k(s^{-1})$
OMePTAC-BODIPY	-0.10	0.30	0.29	0.59	1.2×10^{11}	-1.53	0.33	0.29	0.62	1.5×10^8
PTAC-BODIPY	-0.16	0.30	0.29	0.59	3.0×10^{11}	-1.47	0.34	0.29	0.63	1.2×10^8
PBI-BODIPY	-0.69	0.22	0.29	0.51	3.7×10^{12}	-0.94	0.26	0.29	0.55	4.5×10^{11}

Table 1. Driving forces, reorganization energies and rates for the charge separation and charge recombination processes. The electronic coupling is 1.7×10^{-2} eV and 2.2×10^{-2} eV for charge separation and charge recombination processes, respectively.

Because the quantum yields of 1O_2 of the dyads are very low, we perform our calculation from Marcus formula in D^+A to D^+A^- process. The calculated parameters for both the charge separation and charge recombination channels are listed in Table 1. It is clearly shown that reducing the electron affinity of acceptor units in these dyads will lower the charge separation rates largely, for example, the k_{CS} of **PBI-BODIPY** is $3.7 \times 10^{12} s^{-1}$, while the k_{CS} of **OMePTAC-BODIPY** is $1.2 \times 10^{11} s^{-1}$. In spite of that the k_{CS} of PTAC dyes are slower than that of PBI linked dye, the difference between $k_{CS}(10^{11} s^{-1})$ and $k_{CR}(10^8 s^{-1})$ of PTAC dyes are much bigger, while for **PBI-BODIPY**, the predicted rate for charge separation is one order larger than charge recombination rate, for the electron transfer process is in the Marcus inverted region wherein the increasing exergonicity imposes an additional activation barrier.

Conclusion

In summary, we have presented the synthesis of three novel conjugated dyes based on BODIPY-erylene tetracarboxylic derivatives which possess broad absorption with high absorption coefficients both in visible light and near-infrared regions. The LUMO energies of the dyes are precisely

controllable through the changing of acceptor units while the HOMOs are mainly dependent upon the structure of the BODIPY cores. The quantum yield of singlet oxygen of **OMePTAC-BODIPY** and **PTAC-BODIPY** were 3% and 2% respectively, while **PBI-BODIPY** could not trigger 1O_2 generation. In addition, quantum chemical calculations revealed that although the charge separation rate of PTAC linked dyes are decreased by one order of magnitude than that of **PBI-BODIPY**, while the difference between $k_{CS}(10^{11})$ and $k_{CR}(10^8)$ of PTAC linked dyes are much bigger (1000 times) which will be beneficial to the photoelectric conversion and energy storage process. In view of all these characters, these BODIPY-erylene tetracarboxylic derivatives are hopeful for potential applications in energy conversion and energy storage process, and the device fabrication and measurement based on these dyads are currently under way.

Acknowledgements

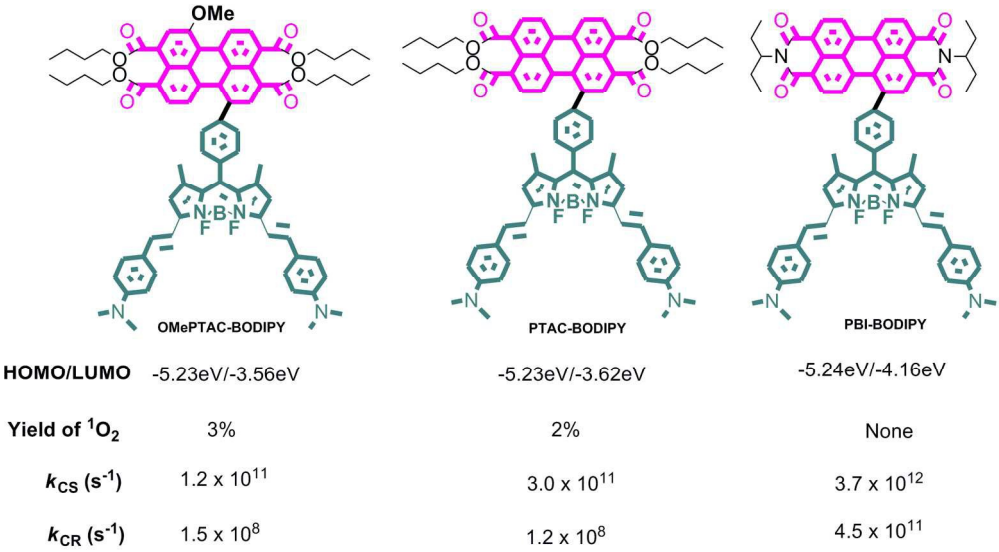
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21442009). We sincerely appreciate Professor Jie Ding of Zhengzhou University for her helpful discussions.

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Three novel dyads were synthesized and subjected to detailed spectroscopic examination and DFT calculation. The dyads comprise perylene tetracarboxylic units and dimethylaminostyryl BODIPY moiety. The rates for the charge separation (k_{CS}) and charge recombination (k_{CR}) were calculated. Comparisons about the physical properties with the changed acceptors were made.



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