Article

DiiodoBodipy-Rhodamine Dyads: Preparation and Study of the Acid-Activatable Competing Intersystem Crossing and Energy Transfer Processes

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Supporting Information

ABSTRACT: Iodo-bodipy/rhodamine dyads with cyanuric chloride linker were prepared with the goal of achieving pH switching of the triplet excited state formation. The pH switching takes advantage of the acid-activated reversible cyclic lactam \leftrightarrow opened amide transformation of the rhodamine unit and the fluorescence resonance energy transfer (FRET). The photophysical properties of the dyads were studied with steady-state and femtosecond/nanosecond time-resolved transient absorption spectroscopies, electro-chemical methods, as well as TD-DFT calculations. Our results show that the model dyad is an efficient triplet state generator under neutral condition, when the rhodamine unit adopts the closed form. The triplet generation occurs at the iodo-bodipy moiety and the triplet state is long-lived, with a lifetime of 51.7 μ s. In the presence of the acid, the rhodamine unit adopts an opened amide form, and in this case, the efficient FRET occurs from iodo-bodipy to the rhodamine moiety. The FRET is much faster ($\tau_{\text{FRET}} = 81 \text{ ps}$) than the intersystem crossing of iodo-bodipy ($\tau_{\text{ISC}} = 178 \text{ ps}$), thus suppressing the triplet



generation is assumed. However, we found that the additional energy transfer occurs at the longer timescale, which eventually converts the rhodamine-based S_1 state to the T_1 state localized on the iodo-bodipy unit.

INTRODUCTION

Photochemical reagents provide excellent spatial control of chemical reactivity, which has been employed in many areas of material science.¹⁻⁵ For example, photodynamic therapy (PDT) utilizes drugs that are active only in the presence of light to selectively target carcinogenic tissue.⁶⁻⁸ However, due to unwanted photosensitivity of patients undergoing PDT therapy,⁶ an additional degree of chemical control is needed. Since cancerous cells exhibit lower pH than the healthy cells,^{6,9,10} the pH-sensitive reagents for PDT are an elegant way to increase the selectivity of PDT. Previous studies have shown that the formation of triplet excited state in model compounds can be controlled by a pH-switchable photoinduced electron transfer (PET) mechanism,9 or a pH-switchable fluorescence resonance energy transfer (FRET) method.¹, Despite this progress, the diversity of molecular motifs of sensitizers with pH-switchable triplet state production is very limited.

In this work, we explore pH-switchable triplet photosensitizers that utilize rhodamine as a pH-sensitive motif. In acidic solution (or protic solvents), rhodamine exists in its opened amide form, but in basic solution or nonprotonic solution, rhodamine exists in the cyclic lactam structure (Scheme 1a).^{11,12} The two structures show drastically different photophysical properties. The opened amide form gives strong absorption at ca. 560 nm, and it is highly fluorescent. On the contrary, the cyclic lactam form gives absorption only in the UV region, and it is colorless and nonfluorescent. Thus, perfect switching of the visible light absorption (switching between colorless and purple) and fluorescence can be achieved upon binding with proper analytes or variation of pH of the solution.^{12,13} However, the applications of this transformation of the molecular structure and the accompanying spectral variation are mainly in the singlet excited state related manifold.¹² To the best of our knowledge, this switching effect has not been used for switching of triplet excited states.

Our approach toward pH-switchable triplet sensitizers is to utilize the FRET mechanism, as shown in Scheme 1c. Model compound **B-3** consists of the iodo-bodipy (I-Bodipy) dye (triplet generator),^{14–17} and the rhodamine dye (pH-switchable unit), covalently linked via the cyanuric chloride moiety. At high pH, the rhodamine dye is present in the cyclic lactam form, whose S₁ state is too high in energy and does not interfere with the generation of the triplet state at the iodo-bodipy moiety. At low pH, the rhodamine dye adopts an open amide structure, whose lower energy of S₁ state enables the FRET from I-Bodipy to the rhodamine. We postulated that this

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Scheme 1. Design of the Proposed Dyads for pH-Switchable Triplet State Generation



FRET mechanism would successfully compete with the $S_1 \rightarrow T_1$ intersystem crossing (ISC) at the I-Bodipy moiety, thus shutting off the triplet generation. In addition to compound **B**-3, models **B-1** and **B-2** were prepared to investigate the efficiency of FRET through the cyanuric chloride linker (Scheme 1b).

This manuscript reports a detailed photophysical study of model compounds **B-1**, **B-2**, and **B-3** using time-resolved transient absorption spectroscopy and time-dependent density functional theory (TD-DFT) calculations. Our results confirm that the FRET from I-Bodipy to rhodamine indeed takes place at low pH values. However, the surprising finding of this study is that, at longer times, the additional singlet energy transfer process takes place that eventually leads to the generation of the T_1 state at the I-Bodipy moiety. These results are useful for the future study on the principal photophysics of the external stimuli-activatable triplet photosensitizers.

EXPERIMENTAL SECTION

Materials and Equipment. All the chemicals are analytically pure and were used as received. Solvents were dried and distilled prior to use. ¹H and ¹³C NMR spectra were recorded on a Bruker 400/500 MHz spectrophotometer (CDCl₃ as solvent, TMS as standard for which $\delta = 0.00$ ppm). High-resolution mass spectra (HRMS) were determined with ESI-Q-TOF MS spectrometer.

Synthesis and Characterization. Synthesis of Compound 1. 4,4-Difluoro-8-(4-aminophenyl)-3,5-dimethyl-4-bora-3a,4a-diaza-s-indacene (abbreviated as 8-(4'-aminophenyl) Bodipy) (100 mg, 0.169 mmol) was added to a suspension of anhydrous K_2CO_3 (0.12 g, 0.87 mmol) in dry THF (30 mL).

The mixture was stirred in an ice bath at 0 $^{\circ}$ C under N₂ atmosphere for 5 min before addition of cyanuric chloride (31.2 mg, 0.169 mmol). The temperature of the mixture was allowed to slowly rise to room temperature (r.t.) while being stirred. Completion of the reaction was confirmed by TLC (silica gel, dichloromethane). The reaction mixture was filtered, and the solvent was evaporated under reduced pressure. The solid residue was subjected to column chromatography (silica gel, dichloromethane/petroleum ether 5:1, v/v), and the principal bright orange band was collected. The desired product was isolated as an orange powder (74.9 mg). Yield: 91%. Mp > 250 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.77 (d, 2H, *J* = 12.0 Hz), 7.64 (s, 1H), 7.35 (d, 2H, J = 8.0 Hz), 6.00 (s, 2H), 2.56 (s, 6H), 1.43 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ = 164.00, 155.81, 142.91, 140.47, 136.86, 132.23, 131.47, 129.24, 121.39, 121.07, 14.65. TOF HRMS ESI: Calcd ([C₂₂H₁₉BN₆F₂Cl₂]⁺), m/z = 486.1109; found, m/z = 486.1071.

Synthesis of Compound B-1. At r.t., compound 1 (200 mg, 0.41 mmol) was dissolved in anhydrous CH_2Cl_2 (80 mL) then *N*-iodosuccinimide (NIS, 366 mg, 1.64 mmol) was added in one portion. The mixture was stirred for 5 h. Then the mixture was washed with aqueous $Na_2S_2O_6$ solution (3 × 50 mL, 1 M aqueous solution). The organic layer was dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, CH_2Cl_2). The first band was collected to give the product as a red solid (263.6 mg). Yield: 87.0%. Mp: 193–196 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.81 (m, 2H), 7.74 (s, 1H), 7.32 (m, 2H), 2.65 (s, 6H), 1.45 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ = 164.02, 157.12, 145.11, 140.11, 137.36, 131.60, 130.91, 129.07, 128.84,121.31, 85.88, 17.28, 16.08.

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TOF HRMS ESI: Calcd ($[C_{22}H_{17}BN_6F_2Cl_2I_2]^+$), m/z = 737.9042; found, m/z = 737.9047.

Synthesis of Compound B-2. Under N₂ atmosphere, B-1 (100 mg, 0.135 mmol) and meso(4-aminophenyl)bodipy (45.9 mg, 0.135 mmol) were added to a suspension of anhydrous K₂CO₃ (93.5 mg, 0.675 mmol) in dry THF (15 mL) in a Schlenck tube. The tube was sealed, and the mixture was stirred at 60 °C for 24 h. At the end of the reaction, the mixture was filtered to remove the K₂CO₃ and the solvent was removed on a rotary evaporator. The crude product was subjected to column chromatography (silica gel, dichloromethane). The product was isolated as a red-purple powder (63.2 mg). Yield: 45%. Mp > 250 °C. ¹H NMR (DMSO- d_6 , 400 MHz): δ 10.63 (s, 2H), 7.95–7.85 (m, 4H), 7.40–7.37 (t, 4H, J = 12 Hz), 6.19 (m, 2H), 2.50 (s, 6H), 2.42 (s, 6H), 1.38 (s, 12H). ¹³C NMR (100 MHz, CDCl₃): δ = 164.02, 155.83, 154.68, 144.89, 142.64, 141.91, 131.19, 131.07, 128.35, 121.23, 86.23, 54.74, 16.73, 15.63, 14.11. TOF HRMS ESI-: Calcd $([C_{41}H_{36}B_2N_9F_4CII_2]^+), m/z = 1041.0994;$ found, m/z =1041.0909.

Synthesis of Compound B-3. Under N₂ atmosphere, B-1 (100 mg, 0.135 mmol) and compound 2 (65.6 mg, 0.135 mmol) were added to a suspension of anhydrous K_2CO_3 (37.3 mg, 0.270 mmol) in dry THF (15 mL) in a Schlenck tube. The tube was sealed, and the mixture was stirred at 45 °C for 12 h. At the end of the reaction, the mixture was filtered to remove the K_2CO_3 . The solvent was removed by a rotary evaporator. The crude product was subjected to column chromatography (silica gel, dichloromethane/ethyl acetate, 3:1, v/v). The product was isolated as a red-purple powder (50.1 mg). Yield: 62%. Mp: 179–181 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.95–7.91 (m, 1H), 7.81 (d, 1H, J = 8.0 Hz), 7.72 (b, 1H), 7.49-7.46 (m, 2H), 7.23 (t, 2H, J = 16.0 Hz), 7.10-7.07 (m, 1H), 6.47-6.27 (m, 6H), 3.43-3.21 (m, 12H), 2.66 (s, 6H), 1.63 (s, 1H), 1.47 (s, 6H), 1.21–1.11 (m, 12H). ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 156.70, 153.47, 153.12, 148.79,$ 145.35, 145.22, 141.17, 139.60, 132.74, 131.52, 130.71, 128.80, 128.53, 128.26, 123.82, 122.95, 120.92, 120.31, 108.33, 105.09, 97.55, 85.63, 65.09, 44.45, 29.68, 17.26, 16.03, 12.48. TOF HRMS ESI⁻: Calcd ($[C_{52}H_{52}BN_{10}F_{2}I_{2}ClO_{2}]^{+}$), m/z =1187.2114; found, m/z = 1187.2103.

UV–vis Absorption and Fluorescence Measurement. The steady-state UV–vis absorption and emission spectra were recorded on a UV 2550 spectrophotometer or Agilent 8453A UV–vis spectrophotometer and FR 5301 PC spectrofluorometer, respectively. For the samples with rhodamine, all samples were treated with TFA (50 μ L, 5 mol/L), and kept for 1 h before measurement. The solvent is DCM/MeOH (9:1). A stock solution of TFA dissolved in MeOH was used. Fluorescence quantum yields were measured with rhodamine B ($\Phi_F = 97.0\%$ in ethanol) as standard. Fluorescence lifetimes were measured with OB920 luminescence lifetime spectrometer (Edinburgh, U.K.).

Femtosecond Time-Resolved Transient Absorption Spectra. The 800 nm laser pulses were produced at a 1 kHz repetition rate by a mode-locked Ti:sapphire laser and regenerative amplifier (Hurricane, Spectra-Physics). The output from the Hurricane was split into pump (85%) and probe (10%) beams. The frequency of the pump beam was sent into an optical paramagnetic amplifier (OPA-400, Spectra Physics) to obtain the desired excitation wavelength. The energy of the pump beam was <300 nJ/pulse. The probe beam was focused into a two-dimensional translated 4 mm CaF₂ crystal for white light continuum generation between 420 and 800 nm. The flow cell (Starna Cell Inc. 45-Q-2, 0.9 mL volume with 2 mm path length), pumped by a Variable Flow Mini-Pump (Control Company), was used to prevent photodegradation of the sample. After passing through the cell at the magic-angle geometry, the continuum was coupled into an optical fiber and input into a CCD spectrograph (Ocean Optics, S2000). The data acquisition was achieved using in-house LabVIEW (National Instruments) software routines. The group velocity dispersion of the probing pulse was determined using nonresonant optical Kerr effect (OKE) measurements. Sample solutions were prepared at a concentration needed to have absorbance of 1.0 at the excitation wavelength.

Nanosecond Time-Resolved Transient Absorption Spectra. The nanosecond time-resolved transient absorption spectra were detected by the LP920 laser flash photolysis spectrometer (Edinburgh Instruments, U.K.) and recorded on a Tektronix TDS 3012B oscilloscope. All the solutions in the experiments were deaerated with argon for ca. 15 min before measurement.

DFT Calculations. The ground state structures of compounds were optimized using DFT with a B3LYP functional and 6-31G (d) basis set. The initial geometries of the compounds were generated by GaussView. The excited-state related calculations (UV–vis absorptions) were carried out with the TD-DFT with the optimized structure of the ground state [DFT/6-31G(d)]. The emission frequencies of the fluorophores were calculated based on the TDDFT optimized S₁ excited state geometry. There are no imaginary frequencies in frequency analysis of all calculated structures. All of these calculations were performed with Gaussian 09W.¹⁸

RESULTS AND DISCUSSION

Design and Synthesis of the Switchable Dyads. The compounds **B-1**, **B-2**, and **B-3** were prepared with the aim of investigating the acid-activatable FRET to compete with the ISC to produce triplet excited states. The building blocks of the compounds are as follows: (i) rhodamine unit as a pH-switchable FRET acceptor; (ii) I-Bodipy unit as a triplet sensitizer, and (iii) cyanuric chloride as a rigid linker. In a previous study, we showed that the efficient triplet state equilibrium can be established in a Bodipy/I-Bodipy dyad connected by a flexible linker.¹⁶ In this work, we used a rigid cyanuric chloride linker, due to the fact that cyanuric chloride reacts readily with amines,²⁰ enabling simple synthetic route toward dyads and triads. In order to prove that the cyanuric chloride linker allows unrestricted intramolecular triplet energy transfer, Bodipy/I-Bodipy dyad **B-2** was designed (Scheme 1).

Compound B-3 contains both the pH-switchable rhodamine and I-Bodipy moieties and is used in this study to evaluate the pH-switchable FRET mechanism. When rhodamine is in the closed lactam structure (high pH), we expect the photophysics of B-3 to be dominated by ISC at the I-Bodipy moiety to produce triplet excited state. The excited-state behavior of B-3 is expected to change when rhodamine is present in the opened amide form (low pH): the spectral overlap in the absorption and emission spectra of the chromophores should lead to efficient FRET from the I-Bodipy to the opened amide form of rhodamine. This FRET mechanism is postulated to efficiently compete with the ISC of I-Bodipy (Scheme 1c).

Our synthetic procedure starts with the cyanuric chloride as the key intermediate. It is known that cyanuric chloride reacts readily with aromatic or aliphatic amines.²⁰ Thus, amino groups Scheme 2. Synthesis of Model Compounds B-1, B-2, and B-3^a



^{*a*}Key: (a) anhydrous K_2CO_3 , dry THF, 0–5 °C, 1 h. Yield: 91%. (b) NIS and CH_2Cl_2 , 1 h. Yield: 87.0%. (c) Anhydrous K_2CO_3 , dry THF, 60 °C, 24 h. Yield: 45%. (d) Anhydrous K_2CO_3 , dry THF, 45 °C, 12 h. Yield: 62%.

were introduced to the Bodipy or I-Bodipy parts (Scheme 2). Reaction of ethylenediamine with rhodamine B gives the intermediate compound Rh-closed-H. In order to control the stoichiometry, **B-1** was prepared first. Then the reactive intermediate Bodipy-H was used to prepare dyad **B-2**, while Rh-closed-H was used to prepare dyad **B-3**. It should be pointed out that all rhodamine-containing compounds are colorless or light pink because the Rhodamine moiety is in the closed lactam structure. All the compounds were obtained with satisfactory yields.

UV-vis Absorption and Fluorescence Spectroscopy. To evaluate whether FRET occurs in model dyads, we performed UV-vis absorption and fluorescence measurements on model compounds **B-1**, **B-2**, and **B-3**. The UV-vis absorption bands of Bodipy and I-Bodipy moieties appear at 503 and 535 nm, respectively (Figure 1a). This assignment is in



Figure 1. UV–vis absorption spectra of (a) B-1, B-2, and (b) B-3, Rh-closed-H; $c = 1.0 \times 10^{-5}$ M in CH₂Cl₂/MeOH (9:1, v/v), 20 °C.

Table 1. Photophysical Parameters of the Compounds

accord with the observed absorption bands of compounds **B-1** ($\lambda_{max} = 535 \text{ nm}$, due to I-Bodipy²¹) and **B-2** ($\lambda_{max} = 503$ and 535 nm, due to Bodipy and I-Bodipy, respectively). The absorption bands at 535 nm are similar for **B-1** and **B-2** (Table 1), indicating that there is no significant electronic interaction between the two chromophores in **B-2** at the ground state.^{22–27}

The absorption profile of B-3 is pH-dependent, as shown in Figure 1b. In the absence of trifluoroacetic acid (TFA), the rhodamine moiety of B-3 is in its cyclic lactam form that does not exhibit any absorption bands in the visible region.^{12,28,29} In this case, the absorption spectrum of B-3 is dominated by the I-Bodipy moiety with its characteristic absorption band at 535 nm. In the presence of TFA, a new shoulder absorption band at 558 nm developed (Figure 1b), which is attributed to the rhodamine moiety in the opened amide structure. Fitting the absorption of B-3 in the presence of TFA gives two absorption bands, which are in agreement with the absorption of B-3 (No TFA) and the rhodamine compound Rh-open-H, respectively. By comparison of the absorbance of the rhodamine component with that of the reference compound Rh-closed-H, the ratio of the open form/spirolactam form upon addition of TFA is >99:1 (i.e., the spirolactam \rightarrow open amide form transformation is complete).

Interestingly, we found that the transformation of rhodamine moiety from the cyclic to the open form is relatively slow (Figure S10 of the Supporting Information). For **B-3**, the transformation was followed by the change in the absorption at 558 nm, and the rate constant $k = 8.97 \times 10^{-2} \text{ min}^{-1}$ was obtained. In this work, all the photophysical studies were performed only after a mixture of **B-3**, and TFA was left

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	$\lambda_{ m abs} \; (m nm)^a$	ε^{b}	$\lambda_{\rm em} \ ({\rm nm})^{a,c}$	$\Phi_{ ext{F}} \ (\%)^d$	$ au_{ m F} \ ({ m ns})^e$	$ au_{\mathrm{T}} \; (\mu \mathrm{s})^f$
Bodipy	504	8.7	517	71.2 ^h	3.86 ^h	g
Rh-closed-H (TFA)	556 ^c	7.1	577	47.2	3.75	g
B-1	535	8.70	552 ^a	2.9	$0.46^{a}/0.45^{c}$	$76.9^{a}/56.6^{c}$
B-2	503/537	10.2/7.34	523/552 ^{<i>a,c</i>}	7.1	2.99 $(\lambda_{\rm em} = 523 \text{ nm})^a$	130.6 ^{<i>a</i>}
					1.62 $(\lambda_{\rm em} = 552 \text{ nm})^a$	
					2.78 $(\lambda_{\rm em} = 523 \text{ nm})^c$	
					1.04 $(\lambda_{\rm em} = 552 \text{ nm})^c$	
B-3	534	7.15	$552^{a}/580^{c}$	$3.6^{a}/14.5^{c}$	$0.54^{a}/2.53^{c}$	$51.7^{a}/34.4^{c}$

^{*a*}In CH₂Cl₂/MeOH (v/v, 9:1) (1.0 × 10⁻⁵ M). ^{*b*}Molar absorption coefficient. ε : 10⁴ M⁻¹ cm⁻¹. ^{*c*}In CH₂Cl₂/MeOH (v/v, 9:1) (1.0 × 10⁻⁵ M) with 50 μ L 5 M TFA added. ^{*d*}Fluorescence quantum yields. For B-2, the fluorescence quantum yield was determined by taking account two emission bands into the calculation (upon excitation of the energy donor). ^{*e*}Fluorescence lifetimes, the two $\tau_{\rm F}$ for B-2 depends on its two emission wavelength ($\lambda_{\rm em} = 523$ nm and $\lambda_{\rm em} = 552$ nm). ^{*f*}Triplet state lifetimes. ^{*g*}Not applicable. ^{*h*}Literature value.¹⁶

standing for a sufficient amount of time to ensure complete transformation to the opened rhodamine form.

The UV–vis absorption spectra of **B-3** show that the rhodamine moiety exhibits a red-shifted absorption band relative to the I-Bodipy unit, and there is overlap between the emission spectrum of the I-Bodipy unit and the absorption spectrum of the rhodamine part, suggesting that the intra-molecular FRET from I-Bodipy to rhodamine is possible.^{29,30} Similarly, the FRET from Bodipy to I-Bodipy is expected for compound **B-2**.

The FRET efficiency in B-2 and B-3 was further studied using fluorescence emission and excitation spectroscopy (Figure 2). For B-2, the fluorescence of the energy donor



Figure 2. (a) Comparison of the UV–vis absorption and fluorescence excitation spectra of **B-2** ($\lambda_{em} = 560$ nm). (b) Comparison of the UV–vis absorption and fluorescence excitation spectra of **B-3** and **Rh-closed-H+**TFA ($\lambda_{em} = 590$ nm). Spectra are measured after adding 50 μ L TFA (5 M solution in MeOH) and after standing of the solution for 1 h. (c) Change in emission spectra of **B-2** and Bodipy ($\lambda_{ex} = 480$ nm). (d) Change in emission spectra of **B-3** and **Rh-closed-H** (with TFA) ($\lambda_{ex} = 500$ nm). $c = 1.0 \times 10^{-5}$ M in DCM/MeOH (9:1, v/v), 20 °C.

(bodipy part) is significant compared to that of the energy acceptor (I-Bodipy). This result is different from our recent study on the iodo-bodipy dyad, where a more efficient FRET was observed.¹⁹ The less efficient FRET in **B-2** and **B-3** may be due to the less favorable geometry imposed by different linkers. However, compared to the unsubstituted Bodipy-H, the fluorescence emission of the singlet energy donor in **B-2** is substantially quenched, confirming that FRET occurs in **B-2**. The rate constant was estimated as $k_{\rm ET} = 4.9 \times 10^9 \text{ s}^{-1}$ with eq 1:³¹

$$k_{\rm ET} = \left[\frac{\Phi_{\rm PL}(\text{bodipy})}{\Phi_{\rm PL}} - 1\right] / \tau(\text{bodipy}) \tag{1}$$

Compound **B-3** in the presence of TFA exhibits strong fluorescence emission attributed to the rhodamine part, suggesting that the energy transfer from I-Bodipy to Rh-open moiety is efficient. The FRET efficiency in **B-2** and **B-3** was evaluated from fluorescence excitation spectra, as described by Akkaya.²³ For **B-2**, we found that the band at 503 nm in the fluorescence excitation spectrum is weaker than the UV-vis absorption band. Thus, the singlet energy transfer is calculated as 84% by fitting of the spectra. For **B-3**, the singlet energy transfer efficiency is 41.7%. The nonunity FRET may be attributed to the intramolecular electron transfer or the unfavorable orientation of the dipole moments of the chromophores for FRET.

The photophysical properties of the compounds are summarized in Table 1. On the basis of the fluorescence quantum yields and the fluorescence lifetimes, we propose intramolecular singlet energy transfer for dyads **B-2** and **B-3**.

Electrochemical Measurements. The proposed pHswitchable triplet generation in **B-3** can occur only if the photoinduced electron transfer does not compete with the desired energy transfer. In order to evaluate the thermodynamic driving force for the photoinduced electron transfer in **B-3**, cyclic voltammograms of the model's compounds were collected (Figure 3).



Figure 3. Cyclic voltammograms of the dyad **B-3** and related compounds: (a) **Rh-closed-H**, (b) **I-Bodipy**, (c) **Rh-open-H**, and (d) **B-3.** Ferrocene (Fc) was used as an internal reference ($E_{1/2} = +0.64 \text{ V}$ (Fc⁺/Fc) vs standard hydrogen electrode). Voltammograms were collected in deaerated CH₂Cl₂ solutions containing 1.0 mM model compounds, the ferrocene and 0.10 M Bu₄NPF₆ as supporting electrolytes. Reference electrode: Ag/AgNO₃. Scan rate: 0.1 V/s; 20 °C.

The reference compound **Rh-closed-H** exhibits two reversible oxidation potentials at +1.15 and +1.35 V (Figure 3a), while **I-Bodipy** exhibits reversible oxidation and reduction potentials at +1.54 V and -0.83 V, respectively (Figure 3b). **Rh-open-H** gives drastically different CV curves as compared with that of reference compound **Rh-closed-H**. One irreversible reduction band at -0.69 V and a pseudoreversible oxidation band at +1.49 V were observed (Figure 3c). The redox potentials of **B-3** are almost the sum of the potentials for the reference compounds **Rh-closed-H** and **I-Bodipy** (Figure 3d), indicating that there is no substantial interaction between the rhodamine and the I-Bodipy units. The reduction potentials of the compounds are compiled in Table 2.

The free energy changes of the electron separation (CS) process was calculated using the Weller equation (eqs 2 and 3).

 Table 2. Redox Potentials of Bodipy Photosensitizers^a

	E(Ox) (V)	E(Red) (V)
2	+1.15, +1.35	-
Iodo-Bodipy	+1.54	-0.83
Rhodamine B	+1.49	-0.69
B-3	+1.19, +1.34, +1.51	-0.81

^{*a*}With Fc as an internal reference, for which $E_{1/2}$ (Fc⁺/Fc) = +0.64 V vs standard hydrogen electrode. Cyclic voltammetry in Ar saturated CH₃CN containing a 0.10 M BuNPF₆ supporting electrolyte; Counter electrode is Pt electrode; working electrode is glassy carbon electrode; Ag/AgNO₃ couple as the reference electrode. $c[Ag^+] = 0.1$ M. 1.0 mM dyad photosensitizers in CH₃CN, 25 °C. Conditions: 1.0 mM dyad photosensitizers and 1.0 mM ferrocene in CH₃CN, 298 K. The potentials are relative to the standard hydrogen electrode.

$$\Delta G_{CS}^{\circ} = e[E_{OX} - E_{RED}] - E_{00} + \Delta G_{S}$$
(2)
$$\Delta G_{S} = -\frac{e^{2}}{4\pi\varepsilon_{S}\varepsilon_{0}R_{CC}} - \frac{e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{R_{D}} + \frac{1}{R_{A}}\right) \left(\frac{1}{\varepsilon_{REF}} + \frac{1}{\varepsilon_{S}}\right)$$
(3)

where $\Delta G_{\rm S}$ is the static Coulombic energy, which is described by eq 3, e = electronic charge, $E_{OX} =$ half-wave potential for one-electron oxidation of the electron-donor unit, E_{RED} = halfwave potential for one-electron reduction of the electronacceptor unit (in cases when irreversible oxidation peaks occurred in the cyclic voltammograms, the anodic and cathodic peak potentials were used instead of half-wave potentials), $E_{0.0}$ = S_0/S_1 energy difference approximated with the fluorescence emission wavelength, $\varepsilon_{\rm S}$ = static dielectric constant of the solvent, R_{CC} = center-to-center separation distance determined by DFT optimization of the geometry, $R_{\rm CC}$ (B-3) = 20.9 Å, $R_{\rm D}$ is the radius of the electron donor, RA is the radius of the electron acceptor, ε_{REF} is the static dielectric constant of the solvent used for the electrochemical studies, and ε_0 is the permittivity of free space. The solvent used in the calculation of free energy of the electron transfer is CH_2Cl_2 ($\varepsilon_s = 8.93$).

The driving force for the charge recombination (ΔG_{CR}) was calculated using eq 4:³²

$$\Delta G_{\rm CR} = -(\Delta G_{\rm CS} + E_{00}) \tag{4}$$

On the basis of the free-energy changes summarized in Table 3, the photoinduced electron transfer is not likely to occur in the model compound **B-3**. Out of 6 possible electron transfer processes, only two processes exhibit ΔG values that are more negative than -0.1 eV: ¹BDP* \rightarrow RB-c and RB-o \rightarrow ¹BDP* charge transfers. Thus, only these two electron transfer processes are likely to have sufficiently high rates to occur within the excited-state lifetimes of the model chromophores.

Table 3. Driving Forces of Charge Recombination $(\Delta G_{(CR)})$, Charge Separation $(\Delta G_{(CS)})$ and Charge Separation Energy States for the Rho-BDP Dyad B-3 in DCM^{*a*}

electron transfer	$\Delta G_{(\mathrm{CR})}$ (eV)	$\Delta G_{(\mathrm{CS})}$ (eV)	$E_{\rm CS}~({\rm eV})$
RB-c \rightarrow ¹ BDP*	_	_	_
$^{1}\text{BDP*} \rightarrow \text{RB-c}$	-1.92	-0.33	1.92
1 RB-o* \rightarrow BDP	-2.12	-0.03	2.12
$BDP \rightarrow {}^{1}RB-o^{*}$	-2.22	+0.07	2.22
$^{1}\text{BDP*} \rightarrow \text{RB-o}$	-2.22	-0.03	2.22
RB-o \rightarrow ¹ BDP*	-2.12	-0.13	2.12
$^{1}BDP^{*} \rightarrow RB-o$ RB-o $\rightarrow ^{1}BDP^{*}$	-2.22 -2.12	-0.03 -0.13	2.22 2.12

^{*a*}The arrow means the direction of charge transfer.

However, as we will show further in the text, the electron transfer was not observed in B-3.

Femtosecond Transient Absorption Spectroscopy. The energy transfer between bodipy and iodo-bodipy chromophores was previously demonstrated in a covalent dyad containing a flexible linker.^{19,33} In this study, a new type of linker, derived from cyanuric acid, is explored, and the model compound **B-2** was used to evaluate the efficacy of energy transfer between bodipy and iodo-bodipy connected by a rigid cyanuric linker. The transient absorption spectra of **B-2** were obtained upon excitation at two wavelengths: 500 nm (where bodipy unit absorbs) and 532 nm (where iodo-bodipy unit absorbs). The transient spectra (Figure 4) exhibits the following features: bleach bands at 500 and 532 nm, stimulated emission band in the 570–620 nm range, and the excited-state absorption (ESA) in the 620–750 nm range.

When excited at 500 nm, the ground-state bleach band at 500 nm is dominant at early times but depletes over time with a concomitant growth of the 532 nm bleach. This process is indicative of the singlet energy transfer from the bodipy to iodo-bodipy unit. The rate of this process was evaluated to be $k_{\text{FRET}} = 2 \times 10^{11} \text{ s}^{-1}$ ($\tau = 5 \text{ ps}$) by monitoring the kinetics at 502 nm (Figure 5a). This value is close to the previous reports on FRET bodipy-azabodipy dyads, thus confirming that the cyanuric moiety is an excellent covalent linker for the studies of energy transfer processes in dyads and triads.

At later times, the stimulated emission band decays and a growth in the absorption is observed in the 620–750 nm range. This process is assigned to the ISC of the excited state localized on the iodo-bodipy moiety, based on the known absorption spectrum of the T₁ state of iodo-bodipy.^{21,34} The ISC rate was evaluated to be $k_{\rm ISC} = 8 \times 10^9 \, {\rm s}^{-1}$ ($\tau = 120 \, {\rm ps}$) by following the kinetics at 700 nm (Figure 5a).

The excitation at 532 nm eliminates the possibility of FRET, since the initially formed excited state is localized on the iodobodipy, whose S_1 energy is lower than the S_1 energy of bodipy. Thus, the transient absorption spectra exhibit only one predominant bleach band at 532 nm. The stimulated emission band appears at early times, but decays with a growth of absorption in the 620–750 nm range, which is indicative of the ISC process of the iodo-bodipy moiety, analogous to the same process observed upon the 500 nm excitation. The lifetime of the S_1 state is 131 ps (Figure 5b), which is similar to the lifetime observed upon the 500 nm excitation.

An interesting effect was observed at longer time delays: the relative ratio of the 532 and 500 nm bleach bands is changed, indicating another energy redistribution process. The 500 nm signal increases in intensity, which is consistent with the triplet energy transfer from iodo-bodipy to the bodipy moiety. In order to study the kinetics of the intramolecular triplet energy transfer, the transient absorption spectra were subjected to the global analysis (Figure S16 of the Supporting Information). On the basis of the fit results, we evaluated the rate constants of the forward triplet energy transfers from iodo-bodipy to bodipy ($k_{\rm F}$ = $7.0 \times 10^8 \text{ s}^{-1}$) and the backward triplet energy transfer from bodipy to iodo-bodipy ($k_{\rm B} = 5.6 \times 10^8 \text{ s}^{-1}$). Thus, the triplet energy transfer is much slower than the corresponding singlet energy transfer. This behavior is expected because the triplet energy transfer can occur only by a Dexter mechanism, which requires a close contact between the chromophores. $^{35-37}$

To evaluate the energy difference between the two triplet states, the equilibrium constant for the triplet transfer between the bodipy and the iodo-bodipy units was calculated using k_f

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Figure 4. Femtosecond transient absorption spectra of B-2 in DCM/MeOH (9/1, v/v) with excitation at (a) 500 and (b) 532 nm. Arrows indicate spectral changes as time progresses; $c = 1.0 \times 10^{-5}$ M; 20 °C.



Figure 5. Kinetics of the S₁ absorption, ground state bleach, and T₁ excited state absorption for B-2. (a) $\lambda_{exc} = 500$ nm; (b) $\lambda_{exc} = 532$ nm. $c = 1.0 \times 10^{-5}$ M in DCM/MeOH (9/1, v/v); 20 °C.

and $k_{\rm b}$ rates. The value for the equilibrium constant is $K_{\rm eq} = 0.8$, which indicates that the triplet state is slightly more localized on the iodo-bodipy unit in **B-2**. Determination of the $K_{\rm eq}$ value leads to the estimation of the energy gap between the bodipy and iodo-bodipy triplets as 0.006 eV (assuming $\Delta E = -RT \ln K_{\rm eq}$) (e.g., nearly degenerate).

The excited-state behavior of B-3 was studied under two experimental conditions: in the absence of TFA (when the rhodamine unit exists in a closed form) and in the presence of TFA (when the rhodamine unit adopts an open amide form) (Figure 6). When the rhodamine unit adopts a closed lactam form, the excited-state behavior of **B-3** exhibits the same photophysics as the iodo-bodipy unit, which is known to exhibit a singlet excited state lifetime of 100–150 ps due to the ISC (as shown in the photophysics of **B-2**). Indeed, this behavior was observed for **B-3** in the absence of TFA (Figure 7). The fit of the kinetic trace at 700 nm gives the ISC rate of $k_{\rm ISC} = 5.6 \times 10^9 \, {\rm s}^{-1}$ ($\tau = 178 \, {\rm ps}$).

In the presence of TFA, the photophysical behavior is more complex due to multiple possible energy transfer processes. To

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Figure 6. (a) The transient absorption spectra of **B-3** in DCM/MeOH (9/1, v/v) with (red) and without (blue) TFA obtained 10 ns after the 565 nm excitation pulse. (b) The femtosecond transient absorption spectra of **B-3** in DCM/MeOH (9/1, v/v) in the presence of TFA ($\lambda_{exc} = 565$ nm); *c* = 1.0 × 10⁻⁵ M. Inset: kinetics of Rh-open ground-state bleach probed at 571 nm. The sample of **B-3** was kept in TFA solution for 1 h before measurement.



Figure 7. Transient absorption spectra of **B-3** upon excitation at 532 nm in the presence (panel a) and absence (panel c) of TFA. Comparison of kinetic trances in the presence (red traces) and absence (blue traces) of TFA probed at 700 nm (panel b) and 364 nm (panel d); $c = 1.0 \times 10^{-5}$ M. The sample of **B-3** was kept in TFA solution for 1 h before measurement.

facilitate data interpretation, the **B-3** sample was initially excited at 565 nm, where the Rh-open unit absorbs most of the light. The results of this study indicate that the energy of the initially formed S₁ state of Rh-open migrates over time to the T₁ state of the iodo-bodipy moiety. Figure 6a demonstrates this assignment, by showing that the higher amount of the T₁ state of iodo-bodipy is formed when the Rh-open unit is excited. The nanosecond transient absorption spectrum of **B-3** in the absence of TFA exhibits the signature bands of the T₁ state of iodo-bodipy moiety. The sample of **B-3** in the presence of TFA exhibits the same transient spectrum, but the signal is stronger, indicating that excitation of Rh-open unit leads to

additional generation of the T_1 state localized on the iodobodipy unit (sample concentration and pump power were kept constant in two experiments).

To evaluate the kinetics of energy transfer from the S_1 state of Rh-open to the T_1 state of iodo-bodipy, the femtosecond transient absorption spectra of **B-3** in the presence of TFA were collected upon the excitation at the Rh-open absorption band ($\lambda_{exc} = 565$ nm, Figure 6b). The spectral changes are associated with a conversion from the initially formed S_1 state of Rh-open (transient absorption band at 450 nm) to the T_1 state of iodobodipy (transient absorption band at 700 nm). The kinetics of this energy transfer was monitored at 571 nm, the Rh-open ground-state bleach band. The signal decay can be fitted to either biexponential decay or a stretched exponential function. Since the stretched exponential functions are often utilized to describe energy transfer in conformationally flexible dimers,^{38,39} we report here the results of such fit: $\tau = 1.8$ ns, $\beta = 0.7$. The mechanism by which the energy migrates from the S₁ state of Rh-open to the T₁ state of iodo-bodipy is currently not understood. It is known that the ISC process of the Rh-open unit is not efficient,^{13,47} so it is not likely that the mechanism involves the formation of the T₁ state of the Rh-open unit. Probably it is a singlet—triplet energy transfer.⁴⁰

When B-3 is excited at the iodo-bodipy moiety ($\lambda_{exc} = 532$ nm), the initially formed S1 state is localized on the iodobodipy moiety, and it decays via two competing channels: (i) the intersystem crossing to generate the T₁ state of iodobodipy; (ii) energy transfer to the S₁ state of Rh-open, followed by another energy transfer to the T_1 state of iodo-bodipy. For example, Figure 7b compares the kinetics probed at 700 nm (where the T_1 state of iodo-bodipy absorbs) for B-3 in the presence and absence of TFA. In the absence of TFA, only the ISC process occurs and the growth of the signal occurs within 178 ps. In the presence of TFA, the 700 nm signal arises due to the stimulated emission signal of the S1 state of Rh-open and the excited-state absorption signal of the iodo-bodipy T_1 state. At early times, the stimulated emission signal grows due to the energy transfer from the S₁ state of iodo-bodipy to the S₁ state of the Rh-open unit. At later times, the stimulated emission signal decays and T_1 absorption signal grows due to the formation of the T₁ state of iodo-bodipy.

Similar behavior is observed when kinetics was probed at 364 nm, where S₁ states of both Rh-open and iodo-bodipy absorb. In the absence of TFA, the signal decays due to ISC of the iodo-bodipy unit. In the presence of TFA, the growth and decay of the S1 state of Rh-open appears as well. The kinetic traces at multiple wavelengths fit well to the following model: (i) the rate of energy transfer from the S_1 state of iodo-bodipy to the S₁ state of Rh-open fits to the stretched exponential function with the lifetime of $\tau = 81$ ps and the power coefficient $\beta = 0.6$; (ii) the rate of energy transfer from the S₁ state of Rhopen to the T_1 state of iodo-bodipy was fit using the same rates as obtained in the experiments with 565 nm excitation (Figure 6). Thus, the FRET process in B-3 efficiently competes with the ISC process of the iodo-bodipy unit, which confirms that the proposed pH-activatable triplet generation mechanism can take place. At later times, the decay of the Rh-based S1 state takes place.

Nanosecond Transient Absorption Spectroscopy. In order to study the triplet excited states of the compounds, nanosecond transient absorption spectra of the compounds were studied.⁷ For **B-1**, the transient absorption spectrum (Figure 8a) consists of a bleach band at 535 nm and excited-state absorption bands at 450 nm and in the 600–750 nm range. These signature bands are associated with the T₁ state of iodo-bodipy.^{21,34} The triplet excited state lifetime of **B-1** (20.9 μ s, Figure 8b) is much shorter than the iodo-Bodipy alone (57.1 μ s),²¹ suggesting that the cyanuric acid linker increases the rate of nonradiative decay in **B-1**.

The transient absorption spectra of **B-2** (Figure 8c) exhibit two bleach bands at 502 and 532 nm, indicating the presence of two T_1 states, localized on either bodipy or iodo-bodipy parts in **B-2**. This result is in agreement with the femtosecond transient absorption measurements presented earlier, which have shown that the intramolecular triplet energy transfer from iodo-bodipy



Figure 8. (a) Nanosecond time-resolved transient absorption of **B-1**. $c = 1.0 \times 10^{-5}$ M in deaerated CH₂Cl₂/CH₃OH (9:1, v/v). (b) Decay trace of **B-1** at 530 nm after excitation at $\lambda_{ex} = 532$ nm. (c) Transient difference absorption spectra of **B-2**, $c = 1.0 \times 10^{-5}$ M in deaerated toluene and (d) decay curve of **B-2** at 500 nm after excitation at $\lambda_{ex} = 532$ nm; 20 °C.

to the bodipy takes place. Since the bleach bands decay with the same rate constants, we propose that the T_1 states of bodipy and iodo-bodipy part are in the equilibrium. To evaluate the intrinsic triplet excited state lifetime of **B-2** (and eliminate the effect of triplet-triplet annihilation), the lifetime was evaluated at several concentrations of **B-2**, and the extrapolation to infinite dilution afforded an intrinsic lifetime of 464.5 μ s. This long-lived triplet excited state is an important characteristic of **B-2**, since the long-lived triplet excited states are crucial for the application of the triplet photosensitizers in luminescent oxygen sensing,⁴¹⁻⁴⁴ triplet-triplet annihilation upconversion,⁴⁴⁻⁵¹ and photodynamic therapy, etc.^{1,2,52}

The nanosecond transient absorption spectra of B-3 showed a somewhat surprising behavior. The femtosecond experiment presented earlier showed that the efficient FRET occurs in the presence of TFA, thus moving the energy from the iodo-bodipy to the Rh-open moiety. This result was in accord with the pHactivatable mechanism proposed in this study. The nanosecond experiments presented here show that another energy redistribution takes place at a longer timescale, which results in the population of the T_1 state of the iodo-bodipy moiety. These results support the postulations of a singlet-triplet energy transfer from the rhodamine unit to the iodo-bodipy moiety, derived from the femtosecond transient absorption spectra. It is known that rhodamine chromophore gives nonefficient ISC,53 thus triplet-triplet energy transfer from the rhodamine moiety to the diiodoBodipy moiety is ruled out. The following text outlines these results in more detail.

In the absence of TFA, the transient absorption profile of **B-3** (Figure 9a) is typical of the T_1 state of iodo-bodipy.^{21,34} This result is expected, since the Rh-closed unit does not contribute to the photophysics of **B-3**. In the presence of TFA, the spectra hardly show any changes relative to the spectra of **B-3** in the absence of TFA (Figure 8c), suggesting that the T_1 state of iodo-bodipy is populated even when the Rh-unit is present in the open amide form. The T_1 state energy level of rhodamine (1.78 eV) is higher than the bodipy part (1.61 eV).⁵⁴



Figure 9. (a) Nanosecond time-resolved transient difference absorption spectra of **B-3** in the absence of TFA, $c = 1.0 \times 10^{-5}$ M in deaerated CH₂Cl₂/CH₃OH (9:1, v/v). (b) Decay trace of **B-3** in the absence of TFA at 530 nm upon excitation at 532 nm. (c) Transient absorption spectra of **B-3** in the presence of TFA, $c = 1.0 \times 10^{-5}$ M in deaerated CH₂Cl₂/CH₃OH (9:1, v/v) with 50 μ L 5 M TFA added (the solution was left to stand for 1 h before the measurement). (d) Decay trace of **B-3** in the presence of TFA at 530 nm, $\lambda_{ex} = 532$ nm; 20 °C.

Observation of the triplet state for **B-3** in the presence of TFA is surprising, considering that the efficient FRET from iodobodipy to the Rh-open unit was observed at the ultrafast timescale. However, this result is reasonable based on the observation of the energy transfer from the singlet state of rhodamine unit to the triplet state of iodo-Bodipy unit in the femtosecond transient absorption spectra.

DFT Calculations. The photophysical properties of **B-3** in two rhodamine-states were evaluated using time-dependent density functional theory (TD-DFT) calculations. Previously, we and others have shown that TD-DFT calculations are very useful for study of the photochemistry and photophysics of organic chromophores and transition metal complexes.^{51,55–59} When rhodamine unit is present in the closed lactam form, the calculations predict no low-lying singlet excited state localized on the rhodamine part (Figure 10). The first two singlet and triplet states are localized on the iodo-bodipy moiety, which is consistent with the time-resolved measurements presented in the previous sections. The calculated lowest absorption is at 2.7

eV (460 nm), which is higher in energy than the experimental value (2.32 eV, 534 nm), but within the known 0.3-0.5 eV accuracy of the TD-DFT method.

When the rhodamine unit is present in an opened amide form, the calculated excited states show the involvement of the rhodamine unit (Figure 11). The S₁ state is localized on the rhodamine unit, while the S₂ state is localized on the iodobodipy moiety. This calculation is in excellent qualitative agreement with the experimentally obtained results, where it was demonstrated that efficient FRET occurs from iodo-bodipy to the rhodamine-open unit. The calculated transition energies for S₁ (2.6 eV, 477 nm) and S₂ states (2.7 eV, 459 nm) are in a reasonable agreement with the experimental values of 556 nm (2.23 eV) and 534 nm (2.33 eV).

The order of energies is reversed for the triplet excited states of **B-3**, where the T_1 state is located on the iodo-bodipy moiety (Figure 11), while the HOMO-1 \rightarrow LUMO transition is involved in the T_2 state, which is localized on the rhodamine part. Previously with phosphorescence, it was shown that the rhodamine is with a T_1 state energy level of 1.78 eV,⁵⁴ and the Bodipy is with the T_1 state energy level of 1.61 eV.⁵¹ Thus, the theoretical result is in agreement with experimental result that the T_1 state of dyad **B-3** is localized on the bodipy unit.

Jablonski Diagrams. On the basis of the steady-state/timeresolved spectroscopy and TD-DFT calculations, the photophysics involved in the dyads B-2 and B-3 are illustrated in Schemes 3 and 4. For B-2, the excitation of the bodipy moiety generates the S₁ state that undergoes a FRET process to the iodo-bodipy moiety with a rate constant of $k_{\text{FRET}} = 2 \times 10^{11} \text{ s}^{-1}$ (τ = 5 ps). Then, the ISC of the iodo-bodipy part generates the T₁ state on iodo-bodipy with a rate constant of $k = 8 \times 10^9 \text{ s}^{-1}$ (τ = 120 ps). At the longer timescale, the downward triplettriplet energy transfer (TTET) to the bodipy part takes place with a rate constant of $k = 7.0 \times 10^8 \text{ s}^{-1}$ ($\tau = 1.4 \text{ ns}$), while the reverse upward TTET occurs with the slightly slower kinetics of $k = 5.6 \times 10^8 \text{ s}^{-1}$ ($\tau = 1.8 \text{ ns}$). The two triplet states decay with an equal rate constant ($\tau_{\rm T}$ = 130.6 μ s, at 1.0 × 10⁻⁵ M) to recover the molecule in the ground state. The photophysical behavior of B-2 shows that the efficient energy transfer processes can occur in bodipy dyads connected by a rigid cyanuric acid linker. The data presented here do not rule out the possibility that the energy transfer process occurs concurrently with the independent excitation and decay of individual chromophores. Given the possible number of conformations that the dimers can adopt at room temperature solution, it is possible that some conformers favor energy transfer more than the others.



Figure 10. Selected frontier molecular orbitals involved in the excitation and emission of B-3 (with rhodamine in closed form). CH_2Cl_2 was used as the solvent in the calculation (PCM model). The calculations are at the B3LYP/6-31G(d)/LANL2DZ level using Gaussian 09W.



Figure 11. Selected frontier molecular orbitals involved in the excitation and emission of B-3 (Rh-open). Dichloromethane was used as the solvent in the calculation (PCM model). The calculations are at the B3LYP/6-31G(d)/LANL2DZ level using Gaussian 09W.

Scheme 3. Simplified Jablonski Diagram Illustrating the Photophysical Processes Involved in $B-2^a$



 ${}^{a}k_{\rm F}$ is the rate constant of forward triplet energy transfer from the iodo-bodipy unit to the bodipy unit. $k_{\rm B}$ is the backward triplet energy transfer from the bodipy to the iodo-bodipy unit.

The photophysical behavior of **B**-3 is pH-dependent. When the rhodamine moiety adopts the closed lactam structure, the S_1 and T_1 states of the rhodamine unit are significantly higher than the corresponding states localized on the iodo-bodipy part. Thus, the photophysical behavior of **B**-3 is dominated by the ISC process of the iodo-bodipy part (Scheme 4a). When the rhodamine unit adopts an open amide form, the S_1 energy of the rhodamine falls below the S_1 energy of iodo-bodipy, and the efficient FRET is observed. The FRET mechanism was expected in this compound and was postulated as a mechanism for pH-activatable triplet generation. However, our experimental results show that the energy eventually migrates from the S_1 state of rhodamine to the T_1 state of the iodo-bodipy moiety. It is currently not well-understood how this energy transfer process occurs. The energy migration might involve higher triplet states (i.e., T_2 state) of the iodo-bodipy that are close in energy with the S_1 state of the rhodamine unit. This finding indicates that the design of pH-activatable triplet generators requires a careful consideration of energetics of first and higher excited states of the two chromophores.

CONCLUSION

In order to switch the triplet excited state of organic triplet photosensitizers by external stimuli, such as acid or base, we prepared a series of dyad triplet photosensitizers based on rhodamine and iodo-bodipy chromophores, with rhodamine as the pH-activatable moiety to perturb both the singlet and the triplet excited state of iodo-bodipy. The iodo-bodipy moiety serves as the singlet energy donor, as well as the spin converter with the intersystem crossing (ISC) capability. A rigid linker of cvanuric chloride was used for connection of the components in the dyads. The molecular design rationale is to establish an acid-activatable competition between two major photophysical processes of the dyads [i.e., the fluorescence resonance energy transfer (FRET) and ISC]. Using steady-state and timeresolved transient absorption spectroscopy, we confirmed that the FRET is indeed acid-activatable. Femtosecond timeresolved transient absorption spectroscopy confirmed the ultrafast FRET in the dyads (81 ps) and the much slower





^{*a*}[BDP-RB-o] stands for **B-3** with the rhodamine part in the open amide structure. [BDP-RB-c] stands for **B-3** with the rhodamine part in the close amide structure. The component at the excited state was designated with red color. The number of the superscript designated either the singlet or the triplet excited state. Note in ¹[BDP-RB-o], the ISC process of the iodo-Bodipy part is with larger rate constant than the FRET process, with the rhodamine part as the singlet energy acceptor.

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ISC of the iodo-bodipy (178 ps). Thus, the ISC of the iodobodipy unit in the dyads is substantially inhibited by the competitive FRET. However, the femtosecond and nanosecond time-resolved transient absorption spectroscopy show that the triplet state of the iodo-bodipy unit is formed at the longer timescale. The triplet state formation is postulated to involve higher triplet excited states of the iodo-bodipy and probably singlet—triplet energy transfer. Our findings shed a light on an almost unexplored area of the switching of triplet excited states of dyad organic triplet photosensitizers. This study will be useful for future molecular design as well as the investigation on the fundamental photophysical properties of the assemblies of organic chromophores.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, molecular structure characterization, additional spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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