Photochromic Reaction by Red Light via Triplet Fusion Upconversion

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ABSTRACT: Red or near infrared (NIR) light responsive molecules have received much attention for biological and material applications because potentially harmful UV light for materials and cells is not required for the photochemical reactions. Although some molecular designs for photochromic molecules to increase the photosensitivity to red or NIR light have been reported, the strategies are limited to the extension of π -conjugation length and the utilization of charge transfer transition or energy and electron transfers. Triplet fusion is an attractive tool to cause chemical reactions by converting low energy excitation light to high energy upconversion light. However, the efficient use of the high energy of upconversion light is difficult because almost all reported triplet fusion systems rely on re-absorption of upconversion light. Here, we demonstrated the red-light driven photochromism via the triplet fusion of a phenoxyl-imidazolyl radical complex, **Pery26 RPIC**, that has a covalently bonded perylene as an annihilator unit. The femtosecond time-resolved absorption and fluorescence spectroscopy revealed that this photochromic reaction proceeds by the highly efficient singlet energy transfer from the annihilator unit to the photochromic unit. This strategy can be applied not only to the development of visible and NIR light responsive photochromic system but also to various photochemical reactions.

INTRODUCTION

Photochromic molecules that respond to red or near-infrared (NIR) light have advantages such as high penetration inside of biological tissues or various media and no requirement of harmful UV light irradiation to materials and cells, leading to application in biological and material chemistry.¹ Various visible or NIR light responsive photochromic molecules, including negative photochromic ones, have been investigated based on azobenzene,²⁻⁴ spiropyran,⁵⁻⁷ diarylethene,⁸⁻¹¹ donor-acceptor Stenhouse adduct (DASA),¹²⁻¹⁶ imidazole dimer, 44 phenoxyl-imidazolyl radical complex (PIC),¹⁷⁻²⁴ and so on.²⁵⁻³¹ The typical approaches to extend the absorption band to the longer-wavelength region is the extension of π -conjugation length or the introduction of electron donor and withdrawing substituents to reduce the HOMO-LUMO energy gap. However, these approaches sometimes require the time-consuming synthetic procedures and strongly affect the efficiency of the photochromic reaction or the stability of the photochromic isomers.

Triplet fusion upconversion, also termed triplet-triplet annihilation upconversion, is one of the photophysical

processes that converts lower-energy photons into higher energy photons.^{32,33} This methodology has been attracted utilizing the excited singlet state generated by triplet fusion. attention for the application to material and biological sciences because of the high efficiency even under weak light such as sun light and incoherent continuous light,³⁴⁻⁶⁰

compared with the other upconversion methods based the PIC derivatives and shows a sequential photochromism on two-photon absorption and multistep excitation of accompanied with the biradical-quinoidal valence lanthanides.⁴⁵⁻⁴⁷ The triplet fusion system consists of two isomerization following the photo-induced bond breaking chemical species, a triplet sensitizer and an annihilator. to form the transient colored isomers as shown in Scheme The annihilator receives the energy from the excited triplet 1.⁶⁵ The biradical and the quinoidal forms are collectively (T_1) state of the sensitizer via triplet-triplet energy transfer called the open-ring form. Perylene has been known as an (TTET) and excited to the T_1 state. Collision between the efficient annihilator for triplet fusion.⁶⁵⁻⁶⁷ We expect the two T_1 annihilators generates an excited singlet (S_1) state introduction of perylene to the 2-position of the imidazole 8 and a ground (S_0) state of the annihilator, leading to the ring of RPIC results in the efficient energy transfer from the 9 upconversion fluorescence from the S_1 state of the perylene unit to the RPIC unit because the annihilator.⁴⁸ aryl group at the 2-position and the imidazole ring can

Triplet fusion is a powerful tool to realize indirectly interact with each other. The DFT calculations photoexcitation leading to chemical reactions with low of **Pery-RPIC**, perylene and RPIC revealed that the energy reaction with high spatial and temporal resolutions unchanged by the substitution to the RPIC unit (Table S5- because the triplet fusion is a two-photon absorption S_7). In addition, the energy level of the S_1 state of perylene process. Recently, some fascinating photochemical is higher than that of RPIC, leading to the energy transfer reactions by using triplet fusion and upconversion systems to induce the photochromic reaction. have been reported.⁴⁹⁻⁵⁴ However, almost all approaches

are limited to the intermolecular energy exchange between the S_1 state of an annihilator and the S_0 state of a chemical species by the re-absorption of upconversion fluorescence. **The Molecular Structure and the Steady-State Absorption Spectra of Pery-RPIC.** Pery-RPIC was The direct utilization of the S_1 state generated by the triplet synthesis according to Scheme 2 as shown in the fusion is an efficient strategy to overcome such drawbacks, Experimental Section. We carried out X-ray but the reported energy or electron transfer mechanisms crystallography of a single crystal of **Pery-RPIC** to reveal are limited to intermolecular processes.⁵⁵⁻⁵⁷ These the molecular structure (Figure 2a and Table S1). Figure 2b

mechanisms require an addition of a large number of annihilator molecules into the system and lead to inefficient reactions due to the absorption by the substrate or the media. As a proof-of-concept study, we propose light responsive photochromism via triplet fusion

upconversion covalently bonded of an annihilator. photochromic In this molecule strategy, with the a

efficient photochromic reaction would be expected, following the effective energy transfer from the annihilator to the photochromic unit (Figure 1a). 35

In this study, we designed a photochromic system **Figure 2.** (a) ORTEP representation of the molecular

consisting of palladium (⁵⁸II) ⁻⁶¹ as a sensitizer and a *meso*-tetraphenyl structure probability), where the nitrogen atoms are highlighted in of **Pery-RPIC** with thermal ellipsoids (50 %

tetrabenzoporphyrin (PdPhphotochromic phenoxyl-imidazolyl radical complex (PIC) ₄TBP) blue and the oxygen atom is highlighted in red. The

covalently bonded to perylene^{62,63} working as an hydrogen atoms are omitted. (b) UV-vis absorption spectra 40 of **Pery-RPIC** (2.7×10^{-5} M), RPIC (3.8×10^{-5} M) and perylene 41 reversible type (T-type) photochromic molecule (1.2×10^{-5} M) in acetonitrile at 298 K.

generating a colored biradical upon light irradiation and 43 thermally reverts to the initial closed form.⁶⁴ RPIC is one of 44

Scheme 1. Molecular Structures and Photochromic Reactions of RPIC and Pery-RPIC Including the Valence Isomerization Reactions

(a) absorption spectra for different time delay after the excitation with nanosecond laser pulse (energy = 0.5 mJ/mm², pulse width = 5 ns) RPIC (2.5×10^{-5} M) in acetonitrile at 298 K and (b) the kinetic trace in microsecond time region, inset: that in millisecond time region .

shows the steady-state absorption spectra of **Pery-RPIC**, **RPIC** and perylene in acetonitrile. The two absorption bands in visible light region and UV light region can be attributable to the absorption of the perylene unit and the **RPIC** unit, respectively. The red shift of the absorption band of **Pery-RPIC** compared with that of perylene in visible light region indicates that the perylene unit and the **RPIC** unit are arranged orthogonal with each other as

shown in Figure 2a and these two units electronically interact by a spiroconjugation-like effect.^{68,69}

Photochromic Reaction in Microsecond Time

Region. The photochromic reaction of **Pery-RPIC** via the excited singlet state of the perylene unit was investigated by the transient absorption technique using nanosecond laser excitation. Figure 3a shows the transient absorption

spectra of **Pery-RPIC** in acetonitrile after 450-nm nanosecond laser pulse that excites the perylene unit. The

transient absorption spectrum at 0.07 μ s after laser excitation shows a negative signal at 420 nm,

corresponding to the depopulation (bleaching) of the initial closed form. The positive absorption bands in the visible light region are assigned to the formation of the open-ring biradical form (**BR**) because of the similar characteristic absorption bands in visible-NIR light region with those of the previously reported **RPIC**.⁶⁵⁻⁶⁷ From 0.07 to 4.0 μ s, a new positive absorption band at 475 nm is growing concomitantly with the decay of positive

absorption bands >500 nm with an isosbestic point at 499 nm and without any changes of the depopulation band. This thermal spectral change is attributable to the valence isomerization from **BR** to the quinoidal form (**Q**). These two around open-ring at 4.0 μ s, and reached the open-ring the thermal forms equilibrium thermally quantitatively generated from the precursor state. (b)

returned to the initial closed form while keeping the equilibrium within 20 ms (Figure 3b). after the excitation, monitored at 460, 630 and 700 nm.

Ultrafast Excited-State Dynamics. To investigate the photodissociation dynamics of **Pery-RPIC** sensitized by

the perylene unit, we carried out femtosecond transient

absorption spectra until 1 ns of experiments. Figure **Pery-RPIC**4a shows in acetonitrile, the transient

excited with 450-nm femtosecond laser. Just after the excitation, the spectrum at 0.3 ps is characteristic of the depopulation band

Figure 4. (a) Transient absorption spectra of **Pery-RPIC** in

acetonitrile, after the excitation with a femtosecond 450-nm laser

pulse (energy = 2.2 μ J, FWHM = 140 fs) and the steady-state absorption spectrum of **Pery-RPIC** is shown as a filled grey spectrum. Black arrow points the isosbestic point at 648 nm during 5.3–1000 ps, indicating the biradical was

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with the bleaching signal of the S_0 state and the absorption of the S_1 state of the perylene unit with the $S_n \leftarrow S_1$ absorption band at 690 nm accompanied with the $S_0 \leftarrow S_1$ structured stimulated emission (maxima at 480 and 510 nm). The assignment of the absorption band at 690 nm and stimulated emission band to the perylene unit is in

agreement with the results of the literatures, the **Figure 5**. Fluorescence spectra of **Pery-RPIC** ($\lambda_{ex.} = 410$ nm), fluorescence steady state spectrum of perylene (Figure 5) RPIC ($\lambda_{ex.} = 300$ nm) and perylene ($\lambda_{ex.} = 410$ nm) in and the transient absorption spectra for perylene alone acetonitrile at 298 K.

(Figure S6).^{70,71} The first picosecond spectrum slightly the structured stimulated emission signals disappeared decreases without any changes of the shape or maxima in together with the appearance of a broad stimulated the time region from 0.3 to 1.3 ps. This process is assigned emission band with a maximum at 520 nm. This broad to the vibrational relaxation of the hot Frank-Condon state stimulated emission band is similar to the steady- the localized cold excited state of the perylene unit. fluorescence spectrum of **Pery-RPIC** (Figure 5). Because After this relaxation, the absorption band at 690 nm the structured vibrational emission bands observed decreases in a few picoseconds and remains at 5.3 ps with in stimulated emission at 520 nm and that the a broad positive band at 700 nm. At the same time, fluorescence spectrum of **Pery-RPIC** large red-

shift compared with that of perylene, the fluorescent state formed in a few picoseconds is assigned to a partial-charge-transfer excited state (Figure 6). This is in agreement with the slower formation and reduced lifetime for this CT excited state in toluene, compared with those in acetonitrile (Figure S8 and Table S2). This CT excited state decreased in about several tens of picoseconds (Figure 4a) and the spectrum at 100 ps is similar to the characteristic 8 band of the biradical form in the ground state (Figure S7).

The kinetic traces at different wavelengths and the respective fits shown in Figure 4b are reproduced by a sum of three exponential functions and a constant. The

estimated time constants are assigned to the relaxation from the FC state to the localized excited state on the perylene unit (0.26 ± 0.008 ps), the formation of the CT excited state (3.1 ± 0.03 ps) and the relaxation of the CT excited state and the formation of the biradical (18 ± 0.1 ps). **Figure 7**. Fluorescence decays at 495 nm of **Pery-RPIC** and The corresponding decay-associated spectra (DAS) are perylene in acetonitrile ($\lambda_{ex.} = 450$ nm, FWHM = 40 ps). given in Figure S8.

To elucidate whether the 18 ps lifetime component is assigned to the excited or the ground state, the dynamics

of the excited state was also investigated by the **Table 1. Fluorescence Decay Time Constants and femtosecond fluorescence spectroscopy with upconversion Fluorescence Quantum Yields Pery-RPIC in Acetonitrile ($\Phi_{Flu.}$) of Perylene and**

technique. The kinetic trace of the fluorescence at 520 nm is shown in Figure S9. The fluorescence was adjusted by a 25 rise with a time constant of 3.1 ps and a decay with a time

constant of 15 ps. This result indicates that the decay component of 18 ps is a CT excited emissive state. It is

considered from the femtosecond time-resolved absorption measurement that this decay component of 18

ps includes not only the radiative relaxation process but

are not
the
centred
shows a

	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	$\Phi_{\text{Flu.}}$
perylene	–	–	4.1 (100 %)	0.71
Pery-RPIC	0.016 (91 %)	0.059 (8.9 %)	3.0 (0.19 %)	0.01

of PIC derivatives generally proceeds from the S₁ state to the formation of **BR**. Because the C–N bond cleavage, state with ultrafast transient absorption spectroscopy for

anti-bonding character about the C–N bond, the CT photochromic imidazole dimers, the C–N bond breaking excited state of **Pery-RPIC** should relax to the bond proceeds via the excited bond-dissociative state within a 34 dissociative state followed by the formation of **BR**. few hundreds of femtosecond.^{72–74} Therefore, the lifetime 35 However, no signal related to the bond dissociation of the bond-dissociative state of **Pery-RPIC** is too short to 36 dynamics was observed. In the time region from 5.3 ps to 1 observe in this experiment, resulting in the isosbestic point

ns, the observation of the isosbestic point at 648 nm with between the absorption spectra of the CT excited state and 38 low recovery of the depopulation band indicates that the **BR**. The plausible photochromic reaction pathway of **Pery**39 efficiency of the C–N bond breaking reaction to form the **RPIC** is shown in Figure 6.

Figure 6. Plausible photochromic reaction pathway of **Pery-RPIC** upon excitation with visible light. Time constants of 260 fs, 3.1 ps and 18 ps correspond to the internal conversion to the localized excited state of the perylene unit.

to the efficient relaxation to the bond-dissociative state of within a few microseconds. The lifetime of the T₁ state of the RPIC unit. Therefore, the relaxation of the fluorescent PdPh₄TBP in the mixture is much shorter than that of state to the bond-dissociative state is highly efficient. individual PdPh₄TBP (Figure S11). The absorption

Red-light Induced Photochromic Reaction via spectrum at 3.05 μ s can be considered to the generation of Triplet Fusion Upconversion. The ultrafast spectroscopy the T₁ state of the perylene unit of **Pery-RPIC** because of revealed that the photochromic reaction of **Pery-RPIC** is the similarity to the spectrum of the T₁ state with a efficiently sensitized by the S₁ state of the perylene unit. maximum at 490 nm.⁷⁶ Moreover, this spectral change

While the direct excitation of the perylene unit to the S₁ from 0.15 to 3.05 μ s shows isosbestic points at 575 and 660 8 state requires 450-nm light, the excitation energy to the T₁ nm. From these results, it can be considered that the TTET

9 state of the perylene unit is almost half of the energy to the from PdPh₄TBP to **Pery-RPIC** quantitatively occurs in this 10 S₁ state (Table S5). Therefore, the generation of the S₁ state condition. At the time scale of 7–175 μ s (Figure 9b), the 11 via the triplet fusion can be expected. As mentioned in spectrum of the T₁ state of **Pery-RPIC** thermally decreases 12 Introduction, PdPh₄TBP has been known as an effective and then the other signal, which has a sharp absorption

triplet sensitizer. Therefore, we demonstrated the red-light band at 490 nm and a broad one in visible to NIR light induced photochromic reaction via triplet fusion region, remains (red line in Figure 9b). This remained upconversion of **Pery-RPIC**. Figure 8 shows the steady absorption spectrum corresponds to the spectrum of the

biradical is quantitative. In the previous study of the **Fluorescence Lifetime and Quantum Yield**

Measurements. To evaluate the efficiency of the relaxation process from the CT state to the excited C–N 43 bond dissociative state of the RPIC units, the picosecond fluorescence lifetime measurements of **Pery-RPIC** and perylene were carried out. Fluorescence decays of **Pery**46 **RPIC** perylene excited with 450-nm picosecond laser 47 pulse are Figure 7. The decay curve of **Pery-RPIC** 48 includes three decay components with the lifetimes of

0.059 and 3.0 ns while that of perylene includes a component of the lifetime of 4.1 ns (Table 1). The main time constant (τ_1 = 0.016 ns, 91%) corresponds to that of the transient CT state observed by the femtosecond time-resolved spectroscopy (τ = 18 ps). In addition, the fluorescence quantum yield of **Pery-RPIC** was estimated to be 0.01 (Quantaaurus-QY, Hamamatsu Photonics K. K.). According to the results of the femtosecond transient absorption experiments, the low quantum yield can be due

state absorption spectra of **Pery-RPIC** and PdPh₄TBP in open-ring form of **Pery-RPIC** at the equilibrium state toluene. PdPh₄TBP has the absorption peaks at 443 nm and shown in Figure 3, indicating the photodissociation 627 nm. Figure 9 shows the temporal change of the reaction of **Pery-RPIC** is induced by the 635-nm light transient absorption spectra of the mixture of **Pery-RPIC** excitation (Figure 9c). The transient absorption spectrum and PdPh₄TBP after the 635-nm nanosecond laser of the open-ring form was not observed when the T₁ state 21 excitation. The absorption spectrum assigned to the T₁ of PdPh₄TBP was quenched by molecular oxygen (Figure 22 state of PdPh₄TBP is generated by the 635-nm light S₁3). Because the DFT calculation suggests that the energy excitation (green line in Figure 9a)⁷⁵ and it changes to a of the RPIC unit, the TTET from the perylene unit to the level of the T₁ state of the perylene unit is lower than that spectrum with maxima at 495 and 640 nm (blue line) RPIC unit is energetically unfavourable (Table S5–S7). In

25 addition, it can be considered that the C–N bond breaking 26 of **RPIC** would not proceed from the T₁ state as 27 similar with hexaarylbiimidazole (HABI).^{77–79} Therefore, 28 the photochromic reaction of **Pery-RPIC** is proceeded via 29 the S₁ state of the perylene generated by the triplet upconversion between the two triplet excited **Pery**31 **RPIC**. It should be the first example of 32 the efficient photochromic reaction directly state of the annihilator generated by the triplet fusion.

light intensity dependence of the 35 photochromic reaction is examined Generally, 36 the intensity of upconversion emission via triplet fusion 37 shows a change in the excitation light intensity

Figure 8. UV-vis absorption spectra of **Pery-RPIC** and dependence from quadratic to linear with increasing the PdPh₄TBP in toluene. excitation light intensity under the steady-state 40 condition.^{80–82} It is expected that the amount of the

Figure 9. Transient absorption spectra of the mixture solution of **Pery-RPIC** (10^{−3} M) and PdPh₄TBP (3×10^{−5} M) in degassed toluene (a) at 0.15–3.05 μs, (b,c) at 7.0–175 μs after the excitation with 635 nm nanosecond laser pulse (power = 2.7 mJ/pulse, pulse width = 5 ns, at room temperature). (c) Black dot line shows the transient absorption spectrum of **Pery-RPIC** in toluene (1.8×10^{−5} M) assigned to the open-ring form reached the thermal equilibrium between BR and Q (λ_{ex.} = 450 nm, power = 6.2 mJ/pulse, pulse width = 5 ns, at 253 K).

EXPERIMENTAL SECTION

Absorption and Fluorescence Spectroscopy. The absorption were measured by a UV-vis-NIR spectrophotometer (SHIMADZU 3600 Plus). The fluorescence spectra were recorded using a fluorescence spectrometer (HORIBA Ltd., FluoroMax3).

Transient Absorption Measurements in Microsecond Time Scale. The laser flash photolysis

experiments were carried out with a TSP-1000 time-

Figure 10. (a) Kinetic traces of the transient absorbance resolved spectrophotometer (Unisoku). The excitation 11 observed at 490 nm after the irradiation with 635 nm laser pulse at 450 nm (pulse width = 5 ns, frequency = 10 Hz) was

pulse to the solution of **Pery-RPIC** (1.9 mM) and provided by a Continuum Surelite II Q-switched Nd:YAG laser coupled to a Continuum Panther EX OPO. The probe PdPh_4TBP (130 μM) in degassed toluene (pulse width = 5 beam from a halogen lamp (OSRAM HLX64623) was used ns, at room temperature). (b) Double logarithmic plots of the average of the transient absorbance at 490 nm during as the probe beam arranged in an orientation

150–180 μs after the excitation as a function of the perpendicular to the exciting laser beam. The probe beam excitation power. The blue and red lines are guide for slope was monitored with a photomultiplier tube (Hamamatsu 2 and 1, respectively. R2949) through a spectrometer (Unisoku MD200) for the decay profile of the colored species. The excitation photochromic product generated by nanosecond laser intensity of one pulse was estimated by an energy monitor 20 pulse irradiation also shows the similar excitation light (Gentec Electro-Optics MAESTRO). Optical-grade 21 intensity dependence (see Supporting Information). We solvents were used for all measurements.

22 measured the transient absorption spectra by varying the **Transient Absorption Measurements in Picosecond** 23 intensity of the excitation nanosecond laser pulse. Figure **Time Scale.** The femtosecond transient absorption spectra 24 10a shows the kinetic traces of the transient absorbance were recorded on the same setup reported earlier (see for 25 ($\Delta\text{Absorbance}$). $\Delta\text{Absorbance}$ at 150–180 μs is proportional example).^{83,84} The main laser source is a 1-kHz Ti:sapphire 26 to the concentration of the open-ring form because the T_1 laser system that delivered 100 fs (1.1 mJ) pulses at 800 nm. 27 states of PdPh_4TBP and **Pery-RPIC** almost disappear 150 This beam was focused in a 1 mm CaF_2 rotating plate to

28 μs after laser excitation. The plots of $\Delta\text{Absorbance}$ against generate white light continuum probe beam which was 29 the excitation light intensity show the quadratic split into a probe beam and a reference beam. The pump30 dependence in the weak excitation region while it is close excitation pulses (450 nm, FWHM 0.4 mm at the

31 to linear in the intense excitation light region (Figure 10b). This change in the dependence can be described as the sample) were obtained from an OPA (Palitra, excel

32 transition from the second order reaction to the pseudo Continuum). The pump-probe polarization configuration 33 first one due to the high concentration of the T_1 state of was set at the magic angle (54.7°) and the probe pulse was

Pery-RPIC upon intense laser irradiation. delayed in time relative to the pump pulse using an optical delay line (Microcontrol, precision: 0.1 μ m). The

CONCLUSION transmitted light of the probe and reference beam was

We succeeded to demonstrate the red-light driven recorded on two different channels of a multichannel photochromism via the triplet fusion of **Pery-RPIC** that spectrograph equipped with a CCD camera (Princeton 39 has a covalently bonded perylene as an annihilator unit. Instrument). A CuSO_4 solution was placed in front of the 40 Because the energy level of the T_1 state of the annihilator is spectrograph to eliminate the remaining 800 nm, and

lower than that of the photochromic unit, the TTET from Rayleigh scattered light from the pump beam was the annihilator to the RPIC unit is inhibited. In addition, suppressed using a Notch filter (Semrock). The acquisition 43 the femtosecond time-resolved absorption and was control using a homemade LabVIEW program. Each

fluorescence spectroscopy for **Pery-RPIC** revealed that the time delay spectrum is the average of 3000 pump excitation. 45 introduction of the annihilator to the photochromic unit is The transient spectra were also computed with the same

highly efficient for the direct utilization of the excited program. The instrumental response function (IRF) of singlet state of the annihilator to induce the photochromic about 140 fs was estimated measuring the stimulated reaction. The mixture solution of PdPh_4TBP and **Pery** Raman amplification signal from the solvent. All

RPIC shows the photochromic reaction of **Pery-RPIC** by experimental data were corrected from the group velocity

the irradiation of 635-nm light which cannot be directly dispersion wavelengths were fit using IgorPro and based on a global (GVD) and kinetic traces at different absorbed by **Pery-RPIC**. We revealed the photochromic analysis with three exponential functions and a constant reaction is induced via the triplet fusion from the transient convoluted with a Gaussian-shaped pulse of the IRF. absorption spectroscopy and the excitation light intensity

dependence. This molecular design will be also applied to

other photochromic molecules and will open up the moved continuously to avoid any thermal heating, development of the red or NIR light responsive molecules.

accumulation or photo-degradation. Stability of the sample was checked after each experiment.

Time-Resolved Fluorescence Measurements. The pulses and found to be about 100 fs (FWHM). The fluorescence decays from 10 ps to nanosecond were fluorescence decays were thus analysed using a double measured using a time-correlated single photon counting exponential decay convoluted with a Gaussian-shaped (TCSPC) technique picoquant. The details of the set up was FWHM of the IRF. The sample was placed in a 1-mm already described in details elsewhere.⁸⁵ Here the cuvette with an optical density of 0.4 while the solution excitation pulse (450 nm) source was delivered by doubling was flown continuously to avoid photo-degradation effects. (harmonic generator, SHG, APE) a femtosecond **Materials and Reagents.** All of the reactions were

Ti:sapphire laser (900 nm, Coherent Chameleon Ultra II, monitored by thin-layer chromatography carried out on 80 MHz, 180 fs) coupled to a pulse picker (4 MHz). 0.2 mm E. Merck silica gel plates (60F-254). Column

Fluorescence lifetimes were measured using an FT200 chromatography was performed on silica gel (silica gel 60N, Picoquant spectrometer. The emission was collected Kanto Chemical Co., Inc.). NMR spectra were recorded at

through a polarizer set at the magic angle and a Czerny 400 MHz on a Bruker AVANCE III 400 NanoBay 12 Turner type monochromator (0.5 mm slit, bandpass 4 nm) spectrometer. DMSO-*d*₆ and CDCl₃ were used as 13 computer-controlled by the software from picoquant deuterated solvents. ESI-TOF-MS spectra were recorded

(picoharp). The single-photon events were collected by a on a Bruker micrOTOF II-AGA1 spectrometer. Unless cooled (-40°) microchannel plate photomultiplier tube otherwise noted, all of the reagents and reaction solvents R3809U (Hamamatsu) and recorded by a PicoHarp 300 were purchased from Tokyo Chemical Industry Co., Ltd., TCSPC card (PicoQuant). The instrumental response Wako Pure Chemical Industries, Ltd., Sigma-Aldrich Inc., 18 function was recorded using a Ludox solution, and its full Kanto Chemical Co., Inc., and AdipoGen Life Sciences Inc., width at half-maximum ⁴ number was 400f events ps. All reached decays at were the and used without further purification.

collected until the 10 **Preparation of the Mixture Solution of Pery-RPIC**

maximum. The recorded decays were analyzed by the and PdPh₄TBP for the Triplet Fusion. Pery-RPIC (10⁻³ 22 FluoFit software (PicoQuant), i.e. decays were fitted by a M) in the sample solution is 100 times as concentrated as

sum of exponential functions convolved by the measured IRF. The quality of the fit was checked by the reduced χ^2 PdPh₄TBP (3×10⁻⁵ M) for the efficient triplet-triplet energy

(below 1.1), and the weighted residuals and autocorrelation transfer.⁸⁷ The sample solution was degassed by freeze25 function. Quality of the alignment was checked that the pump-thaw cycles in a Schlenk tube and transferred to a 26 decay of the coumarin 153 in acetonitrile can be fitted by a quartz cell (light path length: 1 mm) in a globe box under 27 mono-exponential function. nitrogen atmosphere. Optical-grade solvent was used for

the measurement.

Femtosecond and picosecond fluorescence decays were

Synthesis. The synthetic procedure of Pery-RPIC is

measured using a femtosecond fluorescence upconversion

⁸⁶ The source is a 1 kHz Ti-Sapphire laser system shown in Scheme 2. 1-(3',5'-di-*tert*butyl-4'-hydroxy-[1,1'-

setup.(Spitfire Pro 35F-XP, Spectra-Physics) that delivered 800 biphenyl]-2-yl)-2-phenylethane-1,2-dione (**1**) was

nm (4 mJ, 60-nm bandwidth, FWHM), 35-fs pulses synthesized according to the literature procedures.⁶⁵

(FWHM). The output of the amplifier is used to pump two 3,5-di-*tert*-butyl-2'-(2-(perylene-3-yl)-5-phenyl-1H-

identical two-stage optical parametric amplifiers (OPA) of imidazol-4-yl)-[1,1'-biphenyl]-4-ol (**2**). A suspension of **1** (301

35 white light continuum (Topas-C, Light Conversion) to get mg, 0.73 mmol), 3-perylenecalbaldehyde (225 mg, 0.80

36 the pump beam (magic angle configuration) at 450 nm mmol) and ammonium acetate (1.69 g, 22 mmol) in acetic

37 (about 150 μJ at the sample, 60 fs). Less than 1 percent of acid (10 mL) was stirred for 10 h at 110°C in a sealed tube.

38 the 800-nm amplifier output is used as gate pulses. The The reaction mixture was cooled to room temperature and

39 fluorescence light emitted from the sample was efficiently the mixture was neutralized by aqueous ammonia. The

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collected using an off-axis parabolic mirror, filtered to precipitate was filtered and washed with water and n41 suppress the scattered light, directed and overlapped with hexane, to give crude **2** (524 mg) as an orange solid. The 42 the gate pulse (800 nm, ca. 10 μJ) in a BBO crystal. By crude product was used in next procedures without further 43 tuning the incident angle of these two beams relative to the purification because of the poor solubility.

crystal plane, the sum frequency of the fluorescence light **Pery-RPIC**. A solution of potassium ferricyanide (6.85 g, 45 and the gate pulse was generated. A photomultiplier tube 21 mmol), sodium hydroxide (3.15 g, 56 mmol) in water (37 46 (R1527, Hamamatsu), placed at the exit of a mL) was added to a solution of **2** (crude product 500 mg)

monochromator was used to detect the upconversion in benzene (55 mL). After stirring for 9 h at room

fluorescence signal (heterodyne mode). The IRF was temperature, the resultant mixture was extracted with

determined by cross-correlation between pump and gate benzene. The organic extract was washed with water and

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Scheme 2. Synthetic Scheme of Pery-RPIC

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Figure 2

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Figure 3

84x35mm (300 x 300 DPI)

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Figure 5

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Figure 6

84x44mm (300 x 300 DPI)

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Figure 7

59x59mm (300 x 300 DPI)

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Figure 8

58x45mm (300 x 300 DPI)

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Figure 9

158x42mm (300 x 300 DPI)

Figure 10

84x35mm (300 x 300 DPI)

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Scheme 1

84x39mm (300 x 300 DPI)

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Table of Contents

82x36mm (300 x 300 DPI)