Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

A unique photochromic UV-A sensor protein Rc-PYP interacting with PYP-binding protein

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SI-1. Amino acid sequence and CD spectrum of PYP-Binding protein (PBP)

(a)

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MDIVGQLMTDNGRYTFRSDTLNLRVTGDFFEWVMA   35
AAAEMVGIVARREVDSKIDELQALVEFGEASEIEI   70
DSVKYDAKERFEIIPQCVVTMGRTDYRWVAFEGRA   105
KHCATFDGNFVTRVHDMSMTRNDSFLDNENGVDTSGH 142
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(b)

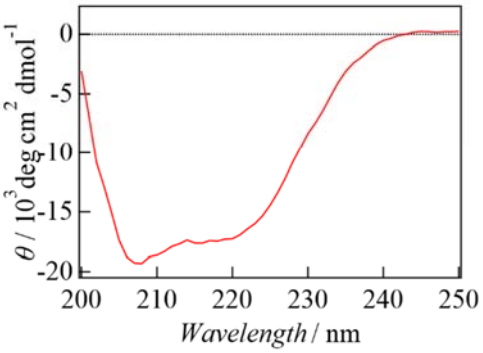

Fig. S1 (a)The amino acid sequence of PBP and (b) CD spectrum of PBP.

SI-2. Dark recovery after UV irradiation

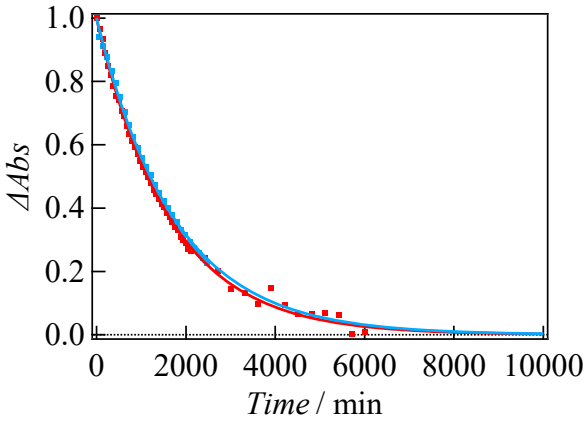

Fig. S2. The dark recovery kinetics of Rc-PYP at 10 μM without (red dots) and with PBP at 100 μM (blue dots) monitored by the absorption at 438 nm. Absorption intensities are normalized by the absorption differences between the dark and light states. The best fitted curves by a single-exponential function (smooth curves) are also shown.

SI-3. Difference traces of Absorption and CD spectra

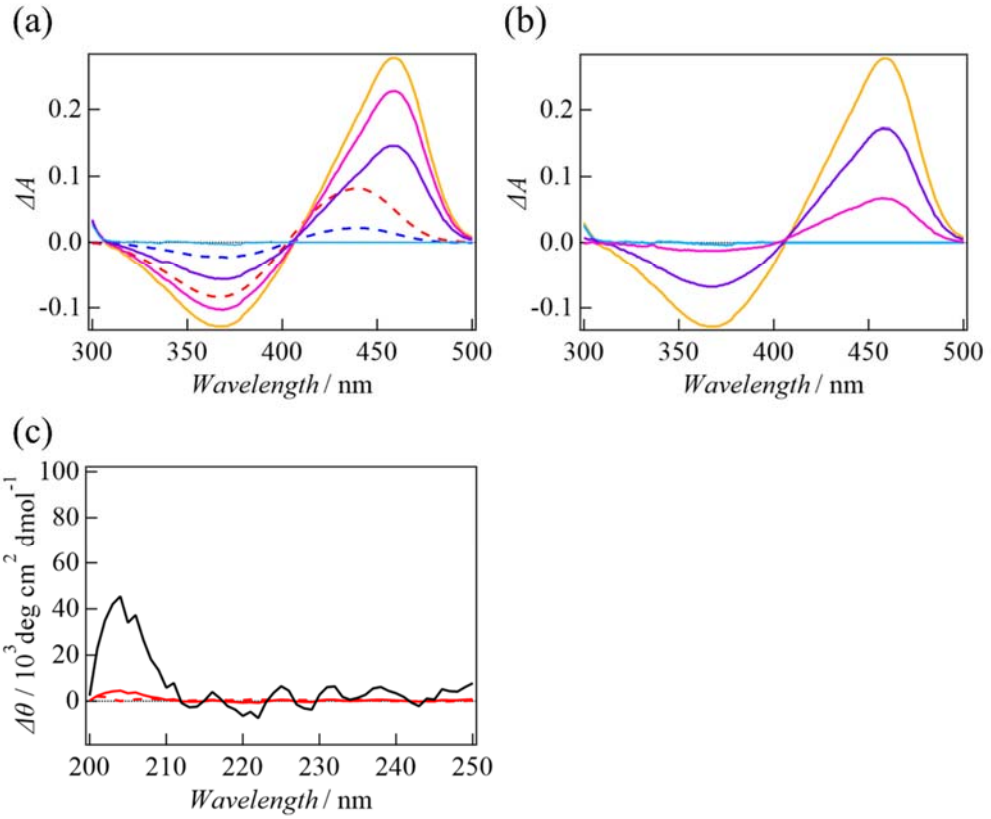

Fig. S3. (a) Absorption difference spectra for the spectra shown in Fig. 1(a) from those in the dark state. The spectra for the PYP(10)-PBP(100) solution in steady state upon BL(480) irradiation (cyan solid line), after irradiation with 360 nm light for 1 s (purple solid line) and 2 s (magenta solid line), and in the steady-state (orange solid line). For comparison, the spectra for the PYP solution (10 μM) in steady-state upon BL(480) irradiation (blue broken line), and steady-state upon irradiation with UV(360) light (red broken line) are also shown. (b) Absorption difference spectra for the spectra shown in Fig. 1(c) from those in the dark state. The spectra for the PYP(10)-PBP(100) solution in the steady state upon irradiation with UV(360) light (orange solid line). The spectral changes upon BL(480) irradiation on the UV(360) pre-illuminated solution for 1 s (purple solid line) and 2 s (magenta solid line), and in the steady state (cyan solid line). and (b) for the spectra in Fig. 1(c). (c) CD difference spectra for the spectra shown in Fig. 7(a); for the solution of [Rc-PYP] = 1 μM and [PBP] = 10 μM (red solid line), and the solution of [Rc-PYP] = 10 μM (red broken line). The CD difference spectrum for the solution of [Rc-PYP] = 1 μM and [PBP] = 10 μM is magnified ten times (black solid line) for a comparison purpose at the same PYP concentration.

SI-4. TrA signal upon 355 nm excitation

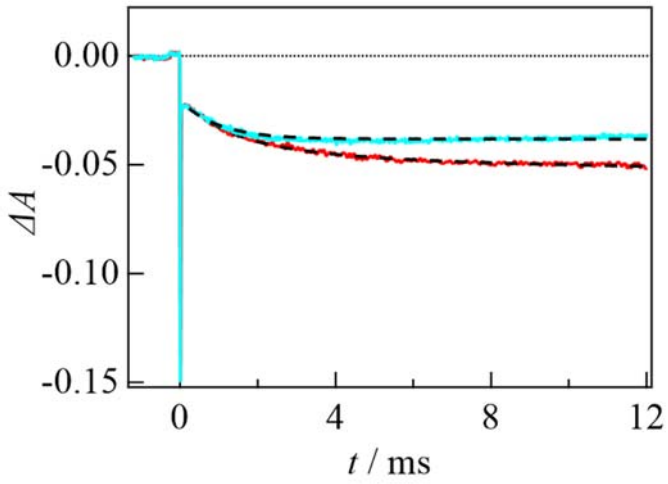

Fig. S4. The TrA signal obtained for the PYP(10)-PBP(100) solution (red curve) and the Rc-PYP solution at 10 μM in the absence of PBP (cyan curve) upon excitation at 355 nm and probed at 370 nm. The best fitted curves by a single-exponential function for the Rc-PYP solution and by eq.(1) for the PYP(10)-PBP(100) solution are shown by the black broken lines.

SI-5. Analytical equation of the diffusion signal based on Scheme1

The time profile of the species grating component based on scheme 1 ($\delta n_{S1}(t)$) may be expressed as;

$$\begin{aligned}\delta n_{S1}(t) = &-\delta n_{UV}\exp(-D_{UV}q^2t) + \delta n_{UV2}\exp\{-(D_{UV2}q^2+k_2)t\}\\
&+\frac{k_2\delta n_{UV*}}{(D_{UV2}-D_{UV*})q^2+k_2-k_3}[\exp\{-(D_{UV*}q^2+k_3)t\}-\exp\{-(D_{UV2}q^2+k_2)t\}]\\
&+\frac{k_2k_3\delta n_{C1}}{(D_{UV2}-D_{UV*})q^2+k_2-k_3}[\frac{1}{(D_{UV2}-D_{c1})q^2+k_2}exp\{-(D_{UV2}q^2+k_2)t\}\\
&-\frac{1}{(D_{UV*}-D_{c1})q^2+k_3}exp\{-(D_{UV*}q^2+k_3)t\}\\
&+\left\{\frac{1}{(D_{UV*}-D_{c1})q^2+k_3}-\frac{1}{(D_{UV2}-D_{c1})q^2+k_2}\right\}exp\{-D_{C1}q^2t\}]\\
&-\delta n_{PBP}\frac{k_2k_3}{(D_{UV2}-D_{UV*})q^2+k_2-k_3}[-\frac{1}{(D_{UV2}-D_{PBP})q^2+k_2}\{exp(-D_{PBP}q^2t)\\
&-exp\{-(D_{UV2}q^2+k_2)t\}\}\\
&+\frac{1}{(D_{UV*}-D_{PBP})q^2+k_3}\{exp(-D_{PBP}q^2t)-exp\{-(D_{UV*}q^2+k_3)t\}\}]\end{aligned} \quad \text{(S1)}$$

where δn_i and D_i (i=UV, UV2, UV*, C1, and PBP) denote the refractive index changes and diffusion coefficients of the i-species, respectively. The subscripts of UV, UV2, UV*, C1, and PBP represent the species of pUV, pUV_2, pUV*, Complex-I, PBP_2, respectively.

SI-6. Analytical equation of the diffusion signal based on Scheme 2 and Scheme 3

The time profile of the species grating component based on scheme 2 (δn_{S2}(t)) is given as;

$$\delta n_{S2}(t) = -\delta n_{C2}\exp(-D_{C2}q^2t) + \delta n_{C2'}\exp\{-(D_{C2'}q^2 + k_{dis})\mathrm{t}\}$$
$$+\frac{2\delta n_{UV}k_{dis}}{(D_{UV} - D_{C2'})q^2 - k_{dis}}[\exp\{-(D_{C2'}q^2 + k_{dis})\mathrm{t}\} - \exp(-D_{UV}q^2t)]$$
$$+\frac{2\delta n_{PBP}k_{dis}}{(D_{PBP} - D_{C2'})q^2 - k_{dis}}[\exp\{-(D_{C2'}q^2 + k_{dis})\mathrm{t}\} - \exp(-D_{PBP}q^2t)] \quad \text{(S2)}$$

where δn_i and D_i (i=C2, C2', UV, and PBP) denote the refractive index changes and diffusion coefficients of the i-species, respectively. The subscripts of C2 and C2' represent the species of Complex-II, the complex of pUV_2-PBP_4, respectively.

The time profile of the species grating component based on scheme 3 (δn_{S3}(t)) is given as;

$$\delta n_{S3}(t) = -\delta n_{C2}\exp(-D_{C2}q^2t) \mp \delta n_{C2''}\exp\{-(D_{C2''}q^2 + k_{dis})\mathrm{t}\}$$
$$+\frac{\delta n_{UV}k_{dis}}{(D_{UV} - D_{C2''})q^2 - k_{dis}}[\exp\{-(D_{C2''}q^2 + k_{dis})\mathrm{t}\} - \exp(-D_{UV}q^2t)]$$
$$+\frac{\delta n_{PBP}k_{dis}}{(D_{PBP} - D_{C2''})q^2 - k_{dis}}[\exp\{-(D_{C2''}q^2 + k_{dis})\mathrm{t}\} - \exp(-D_{PBP}q^2t)]$$
$$+\frac{\delta n_{c1}k_{dis}}{(D_{c1} - D_{C2''})q^2 - k_{dis}}[\exp\{-(D_{C2''}q^2 + k_{dis})\mathrm{t}\} - \exp(-D_{c1}q^2t)] \quad \text{(S3)}$$

where $\delta n_{C2"}$ and $D_{C2"}$ denote the refractive index changes and diffusion coefficients of the complex of pUV-pUV*-PBP_4 in Scheme 3.

SI-7. Simulation of TG signal in dissociation process

The TG signals based on Scheme 2 and Scheme 3 are calculated by eq.(S2) and (S3). The parameters in eq. (S2) was fixed to the value determined by the analysis of q^2 dependence in main text. For calculation of eq.(S3), the same values as the calculation of eq.(S2), δn_{C2}=$\delta n_{C2"}$, and D_{C2}=$D_{C2"}$ are used.

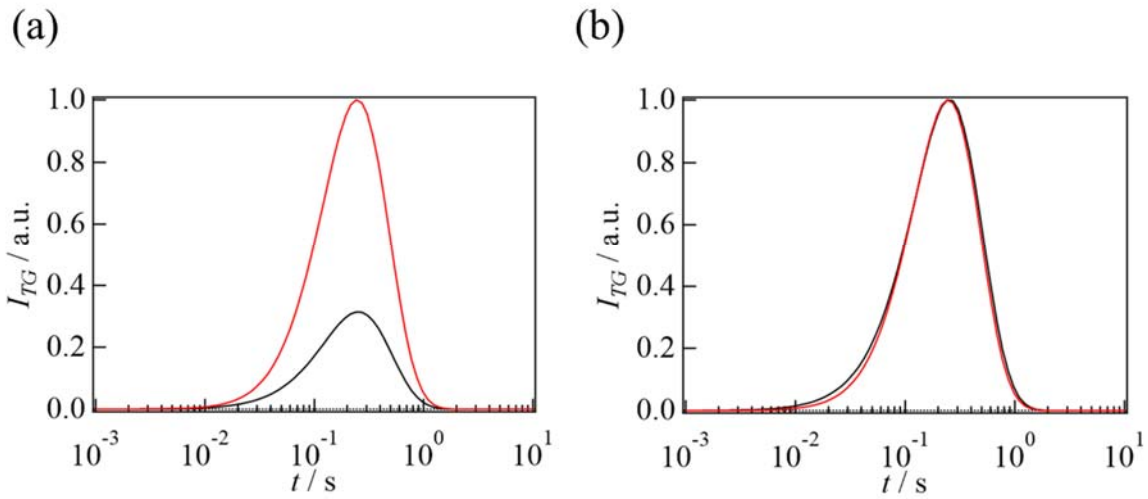

Figure S5. (a) Simulated TG signals based on eq.(S2) (red line) and eq.(S3) (black line). (b) The signals normalized at the peak intensities.