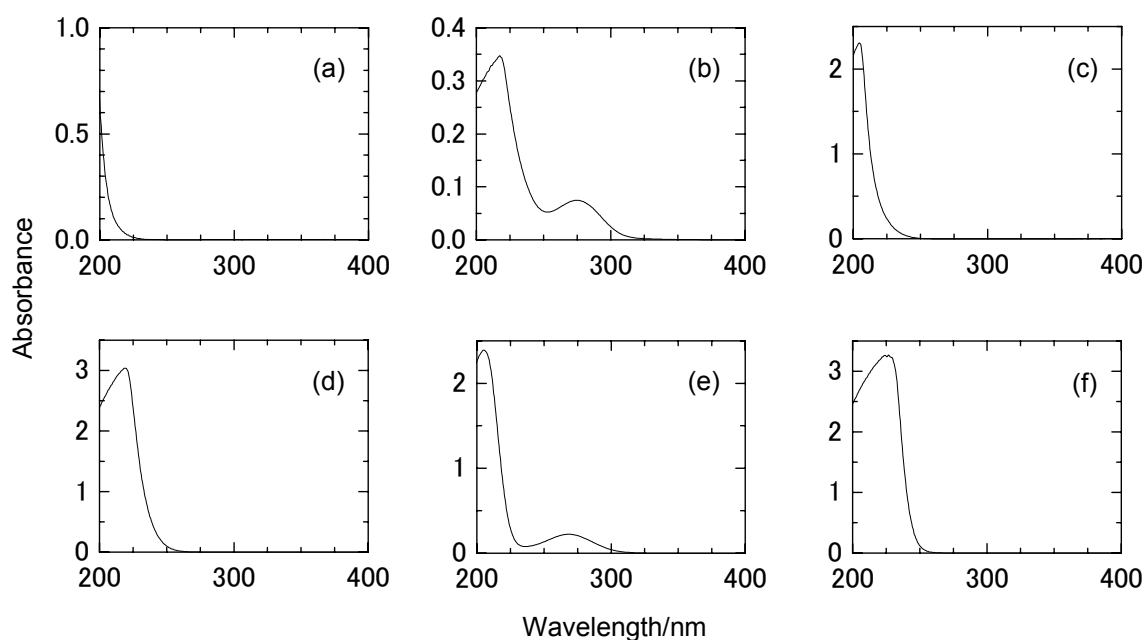


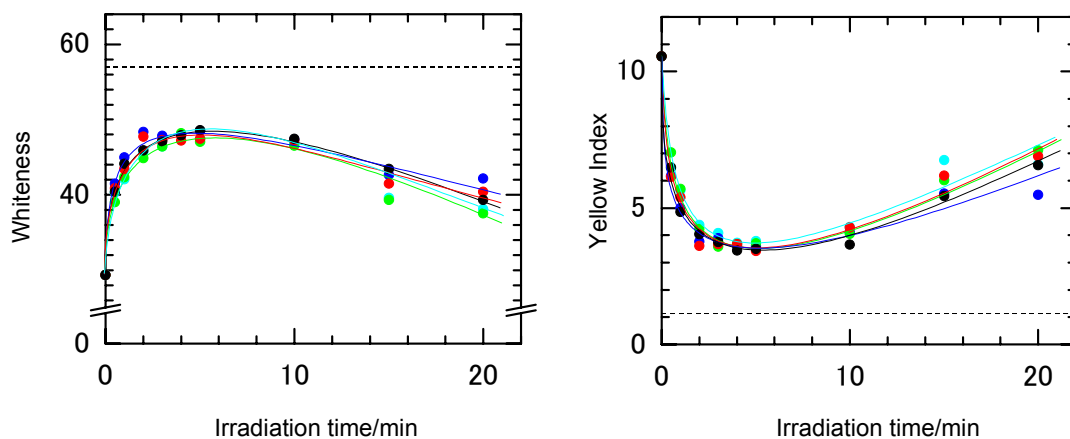
## Supplementary materials

### Reductive total chlorine free photochemical bleaching of cellulosic fabrics

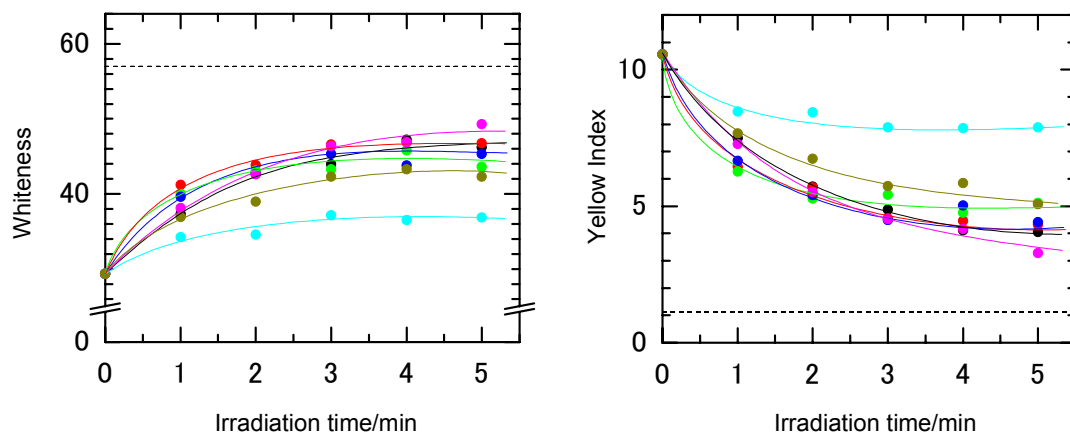
Akihiko Ouchi, Toru Obata, Takeshi Oishi, Hitoshi Sakai, Teruyuki Hayashi, Wataru Ando, and Jun Ito



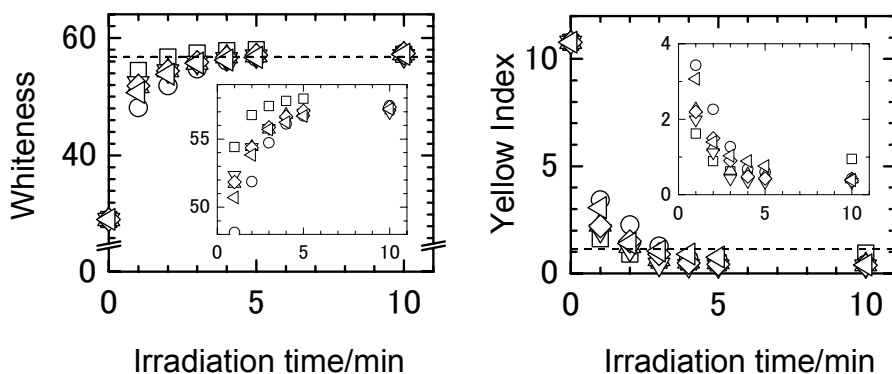
**Fig. S1** UV absorption spectra of (a)  $\text{NaBH}_4$ , (b)  $\text{Na}_2\text{S}_2\text{O}_4$ , (c)  $\text{NaHSO}_3$ , (d)  $\text{Na}_2\text{SO}_3$ , (e)  $\text{H}_2\text{NC(=NH)SO}_2\text{H}$ , and (f)  $\text{HOCH}_2\text{SO}_2\text{Na}$ . Solvent:  $\text{H}_2\text{O}$ . Concentration: 2.5 mM. Optical path: 10 mm.



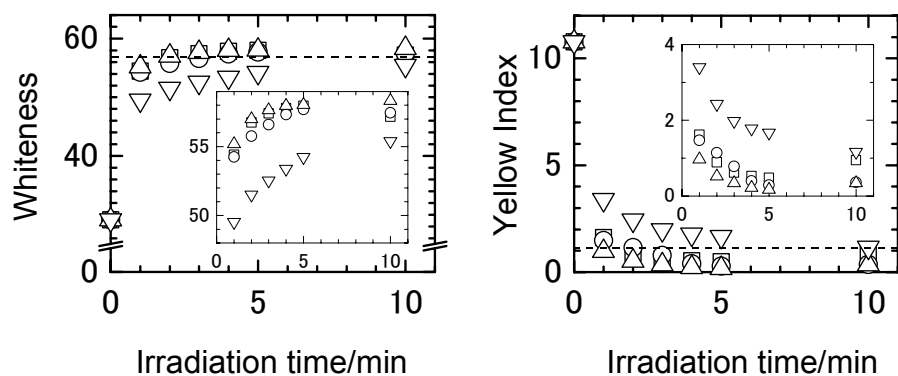
**Fig. S2** Whiteness and yellow index of KrF excimer laser bleached cotton fabrics (**LF**) as a function of irradiation time. Reagents, ● : none (only EtOH); ● :  $(\text{MeO})_3\text{SiH}$ ; ● :  $(\text{EtO})_3\text{SiH}$ ; ● :  $n\text{-Bu}_3\text{SiH}$ ; ● :  $n\text{-C}_8\text{H}_{17}\text{SiH}_3$ . Laser bleaching condition:  $40 \text{ mJ cm}^{-2}$  pulse $^{-1}$ , 5 Hz, room temperature. Reagents: 6 wt% in EtOH. Number of cotton cloths: 1 sheet. Whiteness and yellow index of conventionally bleached fabric (**CF**) are shown in the figures as horizontal broken lines.



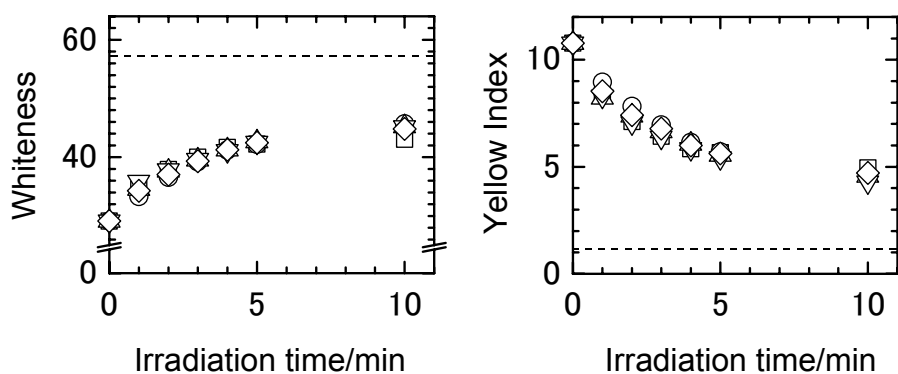
**Fig. S3** Whiteness and yellow index of KrF excimer laser bleached cotton fabrics (**LF**) as a function of irradiation time. Reagents, ● : none (only EtOH); ● :  $(\text{HMe}_2\text{Si})_2\text{O}$ ; ● :  $(\text{HMe}_2\text{SiO})_4\text{Si}$ ; ● :  $\text{Me}_3\text{SiO}(\text{HMeSiO})_{20}\text{SiMe}_3$ ; ● :  $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ ; ● : SM8707 (Dow Corning); ● : SRX310 (Dow Corning). Laser bleaching condition:  $40 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ , 5 Hz, room temperature. Reagents: 6 wt% in EtOH. Number of cotton cloths: 1 sheet. Whiteness and yellow index of conventionally bleached fabric (**CF**) are shown in the figures as horizontal broken lines.



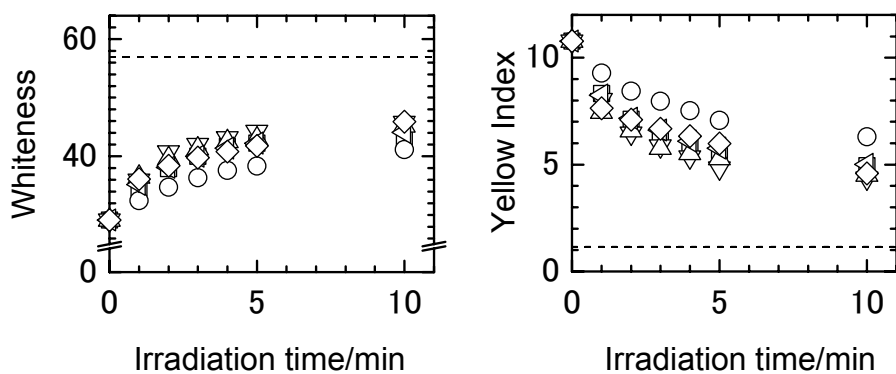
**Fig. S4** Additive effect of amines on the whiteness and yellow index of excimer laser bleached cotton fabrics (**LF**) by NaBH<sub>4</sub> (aq) as a function of irradiation time. Amines, □ : none; ○ : NH<sub>3</sub>; △ : *iso*-Pr<sub>2</sub>NH; ▽ : Et<sub>3</sub>N; ◇ : Et<sub>2</sub>NH; ◁ : EtNH<sub>2</sub>. Laser bleaching condition: KrF laser, 40 mJ cm<sup>-2</sup> pulse<sup>-1</sup>, 5 Hz, 6 wt% NaBH<sub>4</sub> in various solvents (6 wt% amines in H<sub>2</sub>O), room temperature. Number of cotton cloths: 1 sheet. Whiteness and yellow index of conventionally bleached fabric (**CF**) are shown in the figures as horizontal broken lines.



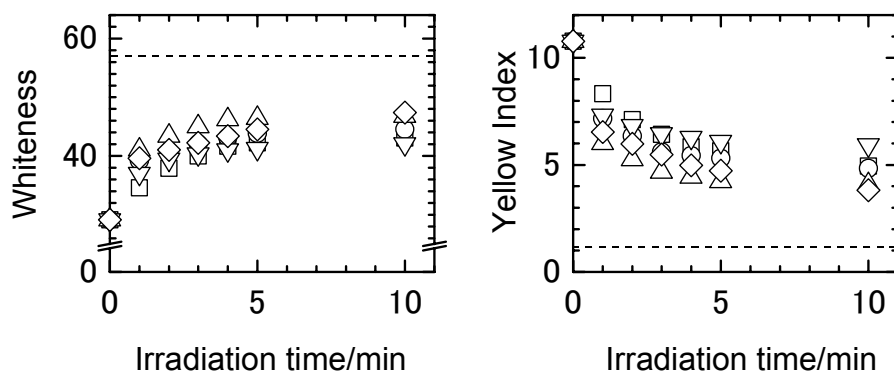
**Fig. S5** Additive effect of ammonium salts on the whiteness and yellow index of excimer laser bleached cotton fabrics (**LF**) by  $\text{NaBH}_4$  (aq) as a function of irradiation time. Ammonium salts,  $\square$  : none;  $\circ$  :  $(\text{NH}_4)_2\text{B}_4\text{O}_7$ ;  $\triangle$  :  $(\text{NH}_4)_2\text{SO}_4$ ;  $\nabla$ :  $(\text{NH}_3\text{OH})_2\text{SO}_4$ . Laser bleaching condition: KrF laser,  $40 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ , 5 Hz, 6 wt%  $\text{NaBH}_4$  in various solvents (6 wt% ammonium salt in  $\text{H}_2\text{O}$ ), room temperature. Number of cotton cloths: 1 sheet. Whiteness and yellow index of conventionally bleached fabric (**CF**) are shown in the figures as horizontal broken lines.



**Fig. S6** Whiteness and yellow index of excimer laser bleached cotton fabrics (LF) in alcohol-H<sub>2</sub>O mixtures as a function of irradiation time. Alcohols, □ : none; ○ : MeOH; △ : EtOH; ▽: *iso*-PrOH; ◇ : *tert*-BuOH. Laser bleaching condition: KrF laser, 40 mJ cm<sup>-2</sup> pulse<sup>-1</sup>, 5 Hz, 6 wt% alcohol in H<sub>2</sub>O, room temperature. Number of cotton cloths: 1 sheet. Whiteness and yellow index of conventionally bleached fabric (CF) are shown in the figures as horizontal broken lines.

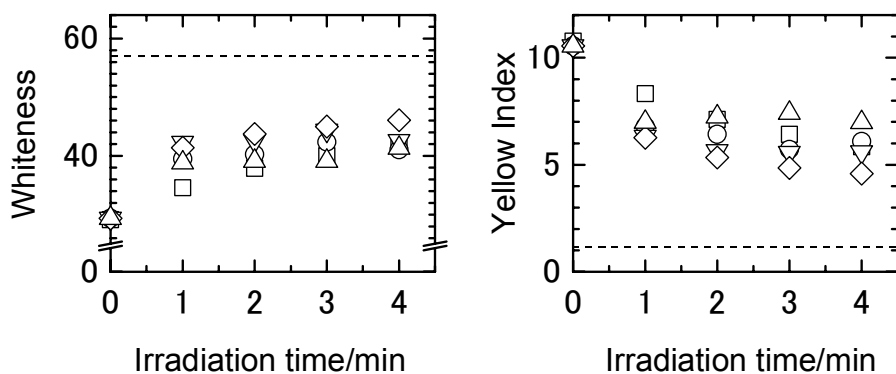


**Fig. S7** Whiteness and yellow index of excimer laser bleached cotton fabrics (**LF**) in amine-H<sub>2</sub>O mixtures as a function of irradiation time. Amines, □ : none; ○ : NH<sub>3</sub>; △ : *iso*-Pr<sub>2</sub>NH; ▽: Et<sub>3</sub>N; ◇ : Et<sub>2</sub>NH; ◁ : EtNH<sub>2</sub>. Laser bleaching condition: KrF laser, 40 mJ cm<sup>-2</sup> pulse<sup>-1</sup>, 5 Hz, 6 wt% amine in H<sub>2</sub>O, room temperature. Number of cotton cloths: 1 sheet. Whiteness and yellow index of conventionally bleached fabric (**CF**) are shown in the figures as horizontal broken lines.

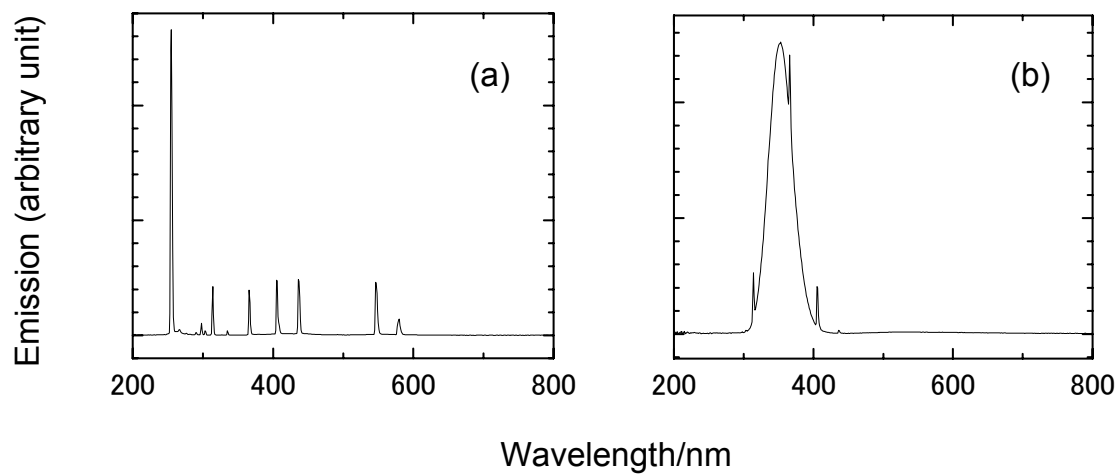


**Fig. S8** Whiteness and yellow index of excimer laser bleached cotton fabrics (**LF**) in ammonium salt- or amide- $\text{H}_2\text{O}$  mixtures as a function of irradiation time. Ammonium salts or amide,  $\square$  : none;  $\circ$  :  $(\text{NH}_4)_2\text{B}_4\text{O}_7$ ;  $\triangle$  :  $(\text{NH}_4)_2\text{SO}_4$ ;  $\nabla$  :  $(\text{NH}_3\text{OH})_2\text{SO}_4$ ;  $\diamond$  :  $\text{HCONH}_2$ . Laser bleaching condition: KrF laser,  $40 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ , 5 Hz, 6 wt% ammonium salt or amide in  $\text{H}_2\text{O}$ , room temperature. Number of cotton cloths: 1 sheet. Whiteness and yellow index of conventionally bleached fabric (**CF**) are shown in the figures as horizontal broken lines.





**Fig. S9** Whiteness and yellow index of excimer laser bleached cotton fabrics (**LF**) in ammonium salt-H<sub>2</sub>O mixtures as a function of irradiation time. Ammonium salts, □ : none; ○ : NH<sub>4</sub>Cl; △ : (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>; ▽ : CH<sub>3</sub>COONH<sub>4</sub>; ◇ : HCOONH<sub>4</sub>. Laser bleaching condition: KrF laser, 40 mJ cm<sup>-2</sup> pulse<sup>-1</sup>, 5 Hz, 6 wt% ammonium salt in H<sub>2</sub>O, room temperature. Number of cotton cloths: 1 sheet. Whiteness and yellow index of conventionally bleached fabric (**CF**) are shown in the figures as horizontal broken lines.



**Fig. S10** Emission spectra of (a) a low-pressure mercury lamp and (b) a black-light fluorescent lamp.