Electronic Supplementary Information (ESI)

Borohydrides oxidation by photoexcited $[\text{UO}_2(\text{CO}_3)_3]^4^-$

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Fig. S1. $^{11}$B NMR spectrum of the sample solution of Fig. 2 after UV-illumination together with that of a borosilicate NMR tube with D$_2$O.

Fig. S2. $^{11}$B NMR spectra of the sample solution of Fig. 4 at different UV irradiation time. B(OH)$_4^-$ as an impurity in NaBH$_3$CN (Purity: 98.5 mol%) was also present in the initial state. The broad band centred at −5 ppm arises from a borosilicate NMR tube (see Fig. S1).
**Fig. S3.** UV-vis absorption spectra of aqueous solution containing $[\text{U}^{VI}O_2(CO_3)_3]^{4-}$ (10.3 mM), $\text{Na}_2\text{CO}_3$ (0.960 M), and $\text{NaN}_3\text{CN}$ (0.693 M) at different time. The sample solution was held at 70°C in the dark.

**Fig. S4.** Optimized structure (left) and spin density $\alpha$–$\beta$ (right) of the lowest triplet state of the uranyl triscarbonate-cyanoborohydride adduct. Hydrogen abstraction by photoexcited $[\text{UO}_2(CO_3)_3]^{4-}$ and charge transfer is observed as similar to borohydride system (Fig. 5). Distances from uranium are shown in Å. Isovalue of the surface is 0.0003 a.u.