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Sulfur forms catenated homoatomic polysulfide dianions S_n^{2-} (commonly, $n = 2-8$) and a persistent radical anion $S_3^{\cdot-}$ (which has been recognized as a chromophore in ultramarine blues). The redox reactivity of polysulfide anions have been studied mainly for the development of alkali metals-sulfur batteries.¹ For example, the electrochemical potentials of the ground state redox couples of $S_3^{\cdot-}/S_3^{2-}$ and $S_4^{\cdot-}/S_4^{2-}$ are identified as -1.35 V and -0.85 V (vs SCE), respectively in DMF (Fig. 1A). Moreover, these species are known to show characteristic absorbance in the visible spectral regions. Namely, the UV-vis absorption spectrum of potassium polysulfide (K_2S_x , US\$0.12/g) in degassed DMSO indicates the presence of $S_3^{\cdot-}$ (λ_{max} at 620 nm), S_4^{2-} (λ_{max} at 440 nm and 330 nm) and S_3^{2-} (λ_{max} at 270 nm) in their steady-states (Fig. 1B). Based on the redox potentials and visible photon absorptions of S_4^{2-} and $S_3^{\cdot-}$ in their ground state, it could be surmised that oxidizable S_4^{2-} potentially serves as a photoexcited reductant, whereas reducible $S_3^{\cdot-}$ functions as a photoexcited oxidant. We recently discovered that these polysulfide anions serve as photoredox catalysts for aryl cross-coupling reactions. The process could be initiated by single-electron-reduction of aryl halides possessing reduction potentials (E_{red}) as low as -2.4 V (vs SCE) by photoexcited S_4^{2-} . The resulting aryl radicals are leveraged for (hetero)biaryl cross-coupling (Fig. 1C), aryl borylation (Fig. 1D), and hydroarylation of alkenes (Fig. 1E) with redox interplay between $S_4^{\cdot-}/S_4^{2-}$ and $S_3^{\cdot-}/S_3^{2-}$ redox couples.²

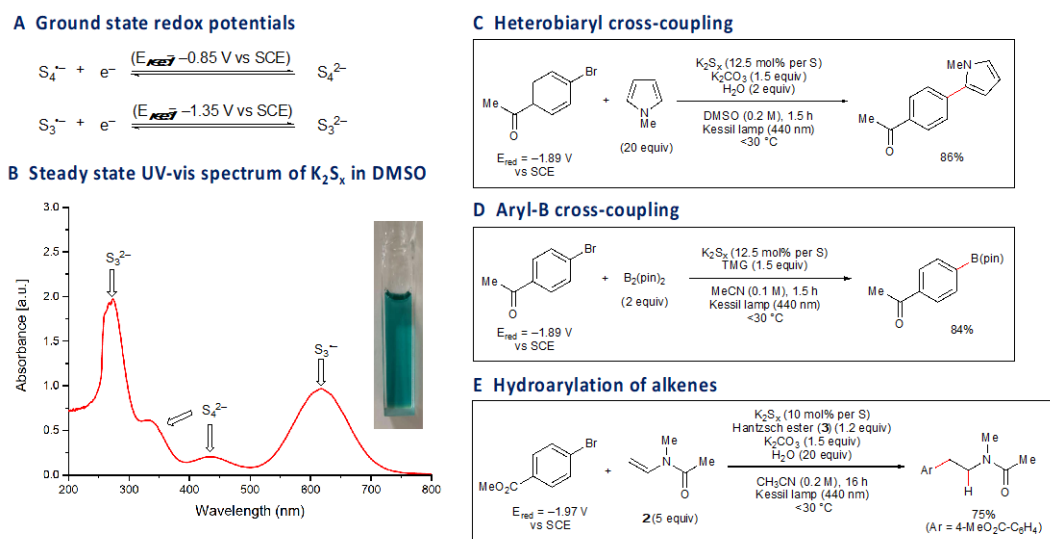


Figure 1.

1. (a) Steudel, R.; Chivers, T., *Chem. Soc. Rev.* **2019**, *48*, 3279. (b) Leghie, P.; Lelieur, J.-P.; Levillain, E. *Electrochem. Commun.* 2002, *4*, 406. 2. (a) Li, H.; Tang, X.; Pang, J. H.; Wu, X.; Yeow, E. K. L.; Wu, J.; Chiba, S. *J. Am. Chem. Soc.* **2021**, *143*, 481. (b) Li, H.; Liu, Y.; Chiba, S. *Chem. Commun.* **2021**, *57*, 6264.

PROFILE

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Shunsuke Chiba earned his PhD in chemistry in 2006 under supervision of Prof. Koichi Narasaka at the University of Tokyo. In 2007, he embarked on his independent career as the faculty of NTU Singapore, where he is currently Professor of Chemistry. His research group focuses on methodology development in the area of synthetic chemistry and catalysis.