

## Electronic Supplementary Information

### Selective photocatalytic aerobic bromination with hydrogen bromide via an electron-transfer state of 9-mesityl-10-methylacridinium ion

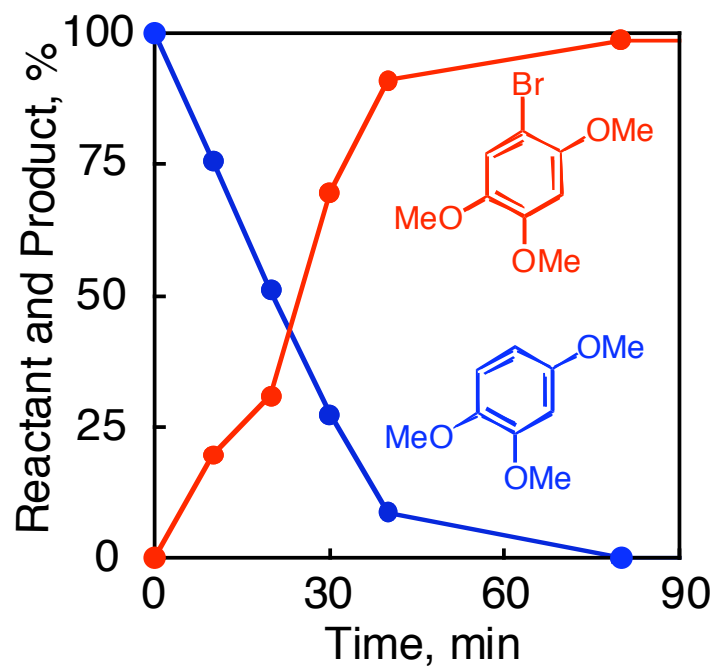
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**Fig. S1.** Time dependence of the reaction of an oxygen-saturated CD<sub>3</sub>CN solution containing [Acr<sup>+</sup>-Mes]ClO<sub>4</sub><sup>-</sup> ( $2.0 \times 10^{-4}$  M), 1,2,4-trimethoxybenzene ( $4.0 \times 10^{-3}$  M) and HBr ( $2.0 \times 10^{-2}$  M) under photoirradiation ( $\lambda > 320$  nm).

**S2:**  $^1\text{H}$  NMR chemical shift of products

2,4,5-Trimethoxybromobenzene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 300 MHz)  $\delta$  7.08 (s, 1H), 6.71 (s, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H) ppm; 2,4,6-trimethoxybromobenzene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  6.27 (s, 2H), 3.83 (s, 3H), 3.80 (s, 6H) ppm; 2,4-dimethoxybromobenzene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.41 (d,  $J = 8.4$  Hz, 1H), 6.59 (d,  $J = 2.4$  Hz, 1H), 6.46 (dd,  $J = 2.4$  Hz, 8.4 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H) ppm; 2,4-dimethoxy-1,5-dibromobenzene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.67 (s, 1H), 6.70 (s, 1H), 3.90 (s, 6H) ppm; 4-bromo-1-methoxynaphthalene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  8.27 (d,  $J = 8.4$  Hz, 1H), 8.15 (d,  $J = 9.0$  Hz, 1H), 7.74 (d,  $J = 8.1$  Hz, 1H), 7.65 (t,  $J = 8.1$  Hz, 1H), 7.59 (t,  $J = 8.1$  Hz, 1H), 6.86 (d,  $J = 8.4$  Hz, 1H), 4.00 (s, 3H) ppm; 2,2'-dibromo-5,5'-bithiophene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.08 (d,  $J = 3.9$  Hz, 2H), 7.00 (d,  $J = 3.9$  Hz, 2H) ppm; 2,3,4-trimethoxybromobenzene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.26 (d,  $J = 9.0$  Hz, 1H), 6.71 (d,  $J = 9.0$  Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H) ppm; 1-bromo-2-methoxynaphthalene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  8.27 (d,  $J = 8.7$  Hz, 1H), 7.95 (d,  $J = 8.7$  Hz, 1H), 7.88 (d,  $J = 8.7$  Hz, 1H), 7.62 (tr,  $J = 8.1$  Hz, 1H), 7.47-7.42 (m, 2H), 4.00 (s, 3H) ppm; 4-bromoanisole:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.42 (d,  $J = 9.0$  Hz, 2H), 6.86 (d,  $J = 9.0$  Hz, 2H), 3.76 (s, 3H) ppm; 2-bromo-3-methylthiophene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.31 (d,  $J = 5.4$  Hz, 1H), 6.85 (d,  $J = 5.4$  Hz, 1H) ppm; 3,4-dimethoxybromobenzene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.06 (d,  $J = 1.5$  Hz, 1H), 7.05 (dd,  $J = 1.5$  Hz, 9.6 Hz, 1H), 6.84 (d,  $J = 9.6$  Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H) ppm; 2-methyl-4-methoxybromobenzene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.43 (d,  $J = 9.0$  Hz, 1H), 6.90 (d,  $J = 3.0$  Hz, 1H), 6.70 (dd,  $J = 9.0$  Hz, 3.0 Hz, 1H), 3.86 (s, 3H), 2.35 (s, 3H) ppm; 4,5-dimethoxy-2-methylbromobenzene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.06 (s, 1H), 6.87 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 2.30 (s, 3H) ppm; 2,2'-dibromoterthiophene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.14 (s, 1H), 7.09 (d,  $J = 3.9$  Hz, 2H), 7.05 (d,  $J = 3.9$  Hz, 2H) ppm; 2,5-dimethyl-4-methoxybromobenzene:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.28 (s, 1H), 6.85 (s, 1H), 3.80 (s, 3H), 2.33 (s, 3H), 2.11 (s, 3H) ppm.