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Electronic Supplementary Information

Iron(III)-Mediated Photocatalytic Selective Substitution of Aryl Bromine by Chlorine with High Chlorides Utilization Efficiency

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Materials and instruments. All reagents and solvents used were obtained commercially and used without further purification. HPLC measurements were made with an Agilent Technologies 1260 Infinity equipped with a DAD detector and a Diamonsil C18(2) column (5μm 250×4.6mm, Dikma) using acetonitrile and water as mobile phase. The produced bromine ion was analyzed by an ICS-900 ion chromatograph with an IonPac AS11-HC column (4×250mm, Dionex). The eluent was 8 mM KOH solution while the flow rate was 1 mL/min and the suppress current was 20 mA. The amounts of Fe(III) and Fe(II) were measured by a U-3900 spectrophotometer (HITACHI).

Typical procedure for the halogen exchange reaction. The photocatalytic reactions were carried out under irradiation by a 300 W high-pressure Xe lamp (PerfitLight Co., Ltd.) (with a filter cut-off light below 360 nm) with continuous stirring in a 50 mL Pyrex glass bottle. To avoid the rapid evaporation, the Pyrex glass bottle was sealed with a rubber stopper wrapped in aluminum foil using the hand crimper and connected to air with an eppendorf tip. A typical reaction system contained 1.0 mM substrate, 5.0 equiv. NaCl and 0.2 mM $FeCl_3$ (purity: 98 %) in 30 mL of acetonitrile. The reaction was monitored by HPLC, and the substrates and products were quantified via the standard curve of the standard substance. The identification and quantification of bromine ion was performed by IC through comparing peak areas with the standard curve. The amounts of Fe(III) and Fe(II) measured by standard literature techniques.[1]

Estimation of quantum efficiency and turnover frequency. The quantum efficiency was estimated on a typical reaction system (contained 1.0 mM substrate, 5.0 equiv. NaCl and 0.2 mM $FeCl_3$ in 3 mL acetonitrile) under the 365 nm UV light irradiation by LED lamp. The light intensity was measured by a radiometer (CEL-NP2000). The intensity of incident light was 270 mW/cm^2 and became 55 mW/cm^2 after absorbed by the system. The irradiating area was 0.785 cm^2. One photon energy at 365 nm is 5.45×10^{-19} J. After 2 h irradiation, the yield and selective of product chlorobenzene were 82.5 % and 95.3 % respectively. The quantum efficiency (QE) and turnover frequency (TOF) were calculated by the following equations.

$$\text{QE} = (\text{mole of chlorobenzene yield}) / (\text{mole of photon absorbed by catalyst}) \times 100\% = 0.074\ \%$$

$$\text{TOF} = (\text{mole of chlorobenzene yield}) / (\text{mole of catalyst}) / \text{reaction time} \times 100\% = 6.30\times10^{-4}\ s^{-1}$$

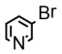
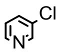
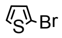
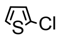
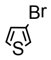
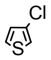
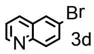
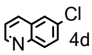
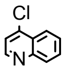
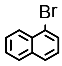
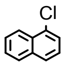
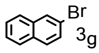
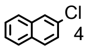
[1] (a) W. Song, W. Ma, J. Ma, C. Chen, J. Zhao, Y. Huang and Y. Xu, *Environ. Sci. Technol.,* 2005, ***39***, 3121; (b) Z. Wang, X. Chen, H. Ji, W. Ma, C. Chen and J. Zhao, *Environ. Sci. Technol.,* 2010, ***44***, 263; (c) H. Tamura, K. Goto, T. Yotsuyanagi and M. Nagayama, *Talanta,* 1974, ***21***, 314.

Table S1 The effects of solvents and chlorine salts on the halogen exchange reaction.[a]

Entry	Solvent	Chlorine salt	Time (h)	Conv. (mol%)	Yield (mol%)	Select. (mol%)
1[b]	water	NaCl	3	75.4	0	0
2[b]	methanol	NaCl	3	0.49	0	0
3[b]	acetonitrile	NaCl	3	90.96	91.7	>99
4[c]	acetonitrile	NaCl	10	97.8	94.3	96.5
5[c]	acetonitrile	LiCl	10	94.1	96.1	>99

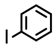
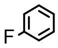
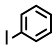
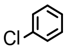
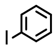
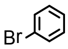
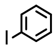
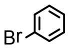
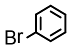
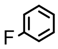
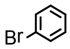
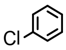
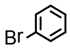
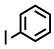
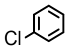
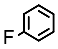
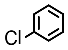
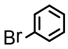
[a] All the reactions were using bromobenzene as substrate. [b] Reaction conditions: 1.0 mM bromobenzene, 5.0 equiv. NaCl and 0.5 mM $FeCl_3$ (purity: 98%) in 30 mL solvent, UV light (λ>360 nm). [c] Reaction conditions: 0.2 mM $FeCl_3$, 1.0 mM bromobenzene, 5.0 equiv. of chlorine salt in 30mL of acetonitrile, UV light (λ>360 nm).

Table S2 The reaction rate constants of heteroaryl and polycyclic aromatic bromide-chloride exchange reactions. [a]

Entry	Substrate 3	Product 4	Reaction rate constant
1	 3a	 4a	0.1248
2	 3b	 4b	0.2819
3	 3c	 4c	0.3053
4	 3d	 4d	0.2597
5	 3e	 4e	0.2351
6	 3f	 4f	0.2783
7	 3g	 4g	0.2740

[a] The reaction conditions were same as typical procedure mentioned above.

Table S3 The exchange reactions of different aryl halogens.[a]

Entry	Substrate	Desired Product	Catalyst	Cat.:Sub. (mol:mol)	Salt	Salt:Sub. (mol:mol)	Reaction (Y/N)
1	 1o	 5	FeF_3	1:2	NaF	25 : 1	N
2	 1o	 2a	$FeCl_3$	1:5	NaCl	5 : 1	Y
3	 1o	 1a	$FeBr_3$	1:5	NaBr	5 : 1	N
4	 1o	 1a	$Fe_2(SO_4)_3$	1:2	NaBr	5 : 1	N
5	 1a	 5	FeF_3	1:2	NaF	25 : 1	N
6	 1a	 2a	$FeCl_3$	1:5	NaCl	5 : 1	Y
7	 1a	 1o	$Fe_2(SO_4)_3$	1:2	NaI	100 : 1	N
8	 2a	 5	FeF_3	1:2	NaF	25 : 1	N
9	 2a	 1a	$FeBr_3$	1:5	NaBr	5 : 1	N

[a] The reaction conditions were same as typical procedure mentioned above.

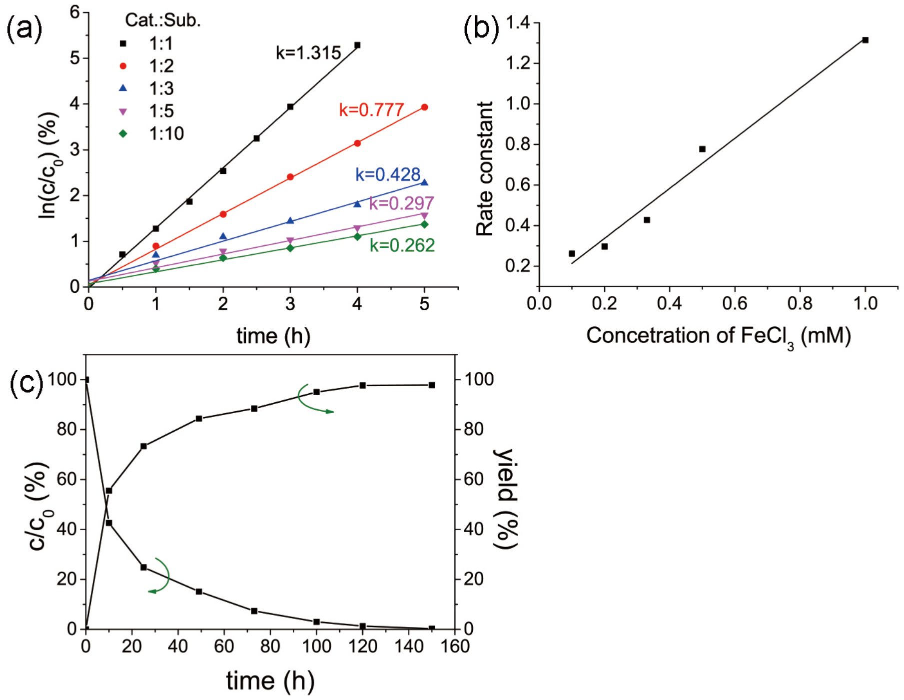


Fig. S1 (a) Influence of catalyst ($FeCl_3$) concentration on the photocatalytic halogen exchange reaction rates. (b) The effect of $FeCl_3$ concentration on the reaction rate constant. (c) The conversion of the bromobenzene and formation of chlorobenzene in the presence of 10 μM catalyst (1% of the substrate). Reaction conditions: 1.0 mM bromobenzene, 5.0 equiv. NaCl in 30 mL of acetonitrile.

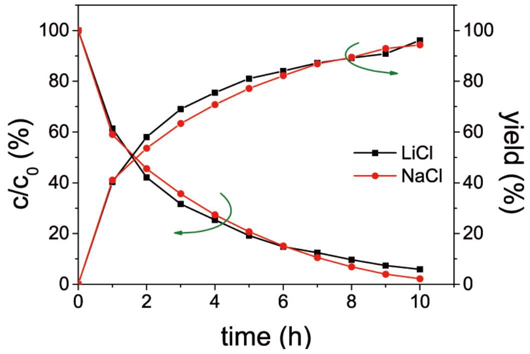


Fig. S2 Halogen exchange reactions using LiCl and NaCl as chlorine source.

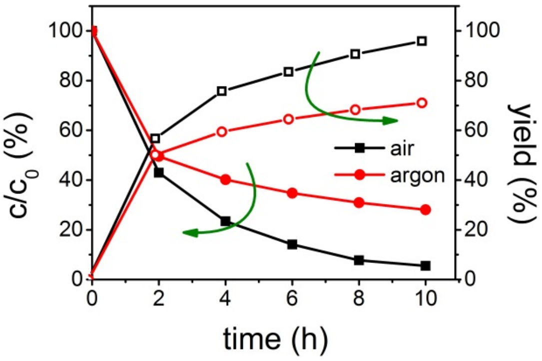


Fig. S3 A comparison on the photocatalytic halogen exchange reactions in the atmospheres of air and argon.

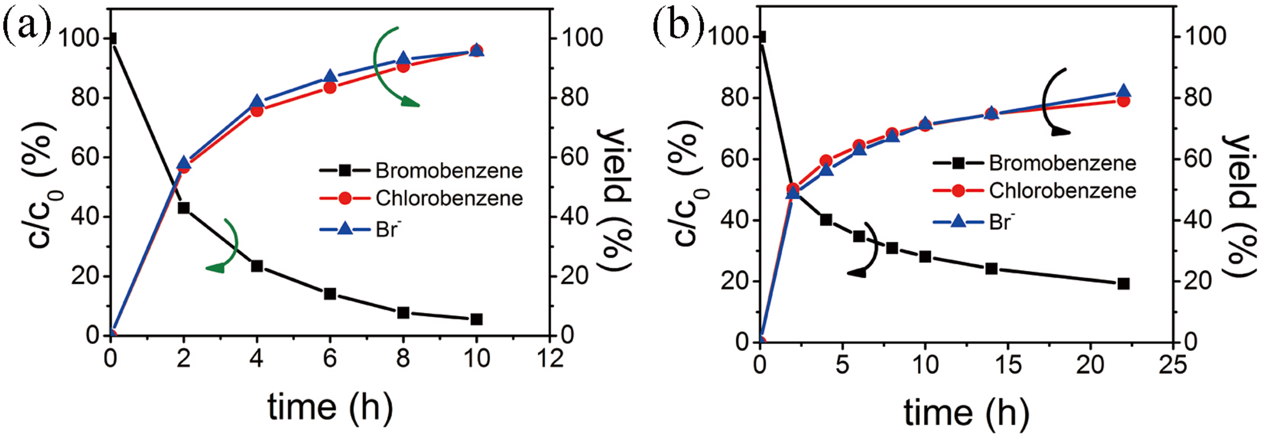


Fig. S4 Release of bromide ion when the reactions are conducted (a) in air and (b) in argon atmosphere. Reaction conditions: 1.0 mM bromobenzene, 5.0 equiv. NaCl and 0.2 mM $FeCl_3$ in 30 mL of acetonitrile.

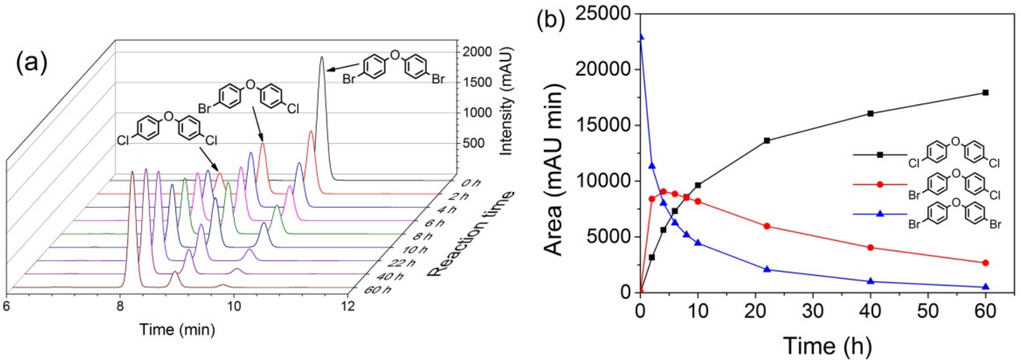


Fig. S5 Stepwise bromide-chloride exchange reaction of 4,4'-dibromodiphenyl ether (**1g**). (a) The HPLC chromatogram after various hours of irradiation. (b) The peak area evolution of stepwise exchange products with irradiation time.

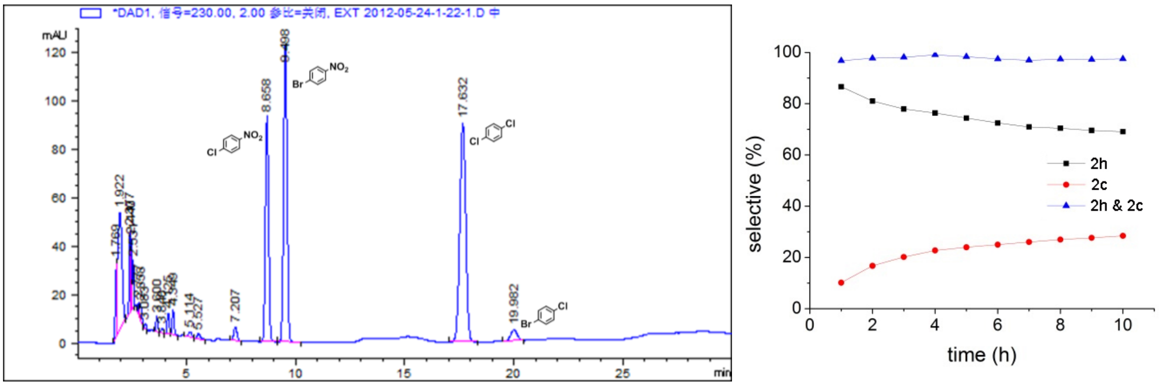


Fig. S6 Analysis of the products of 4-nitro-bromobenzene (**1h**) bromide-chloride exchange reactions (entry 9 in Table 1) by HPLC. Left: the HPLC chromatogram after 22 hours of irradiation; right: the evolution of exchange products with irradiation time.

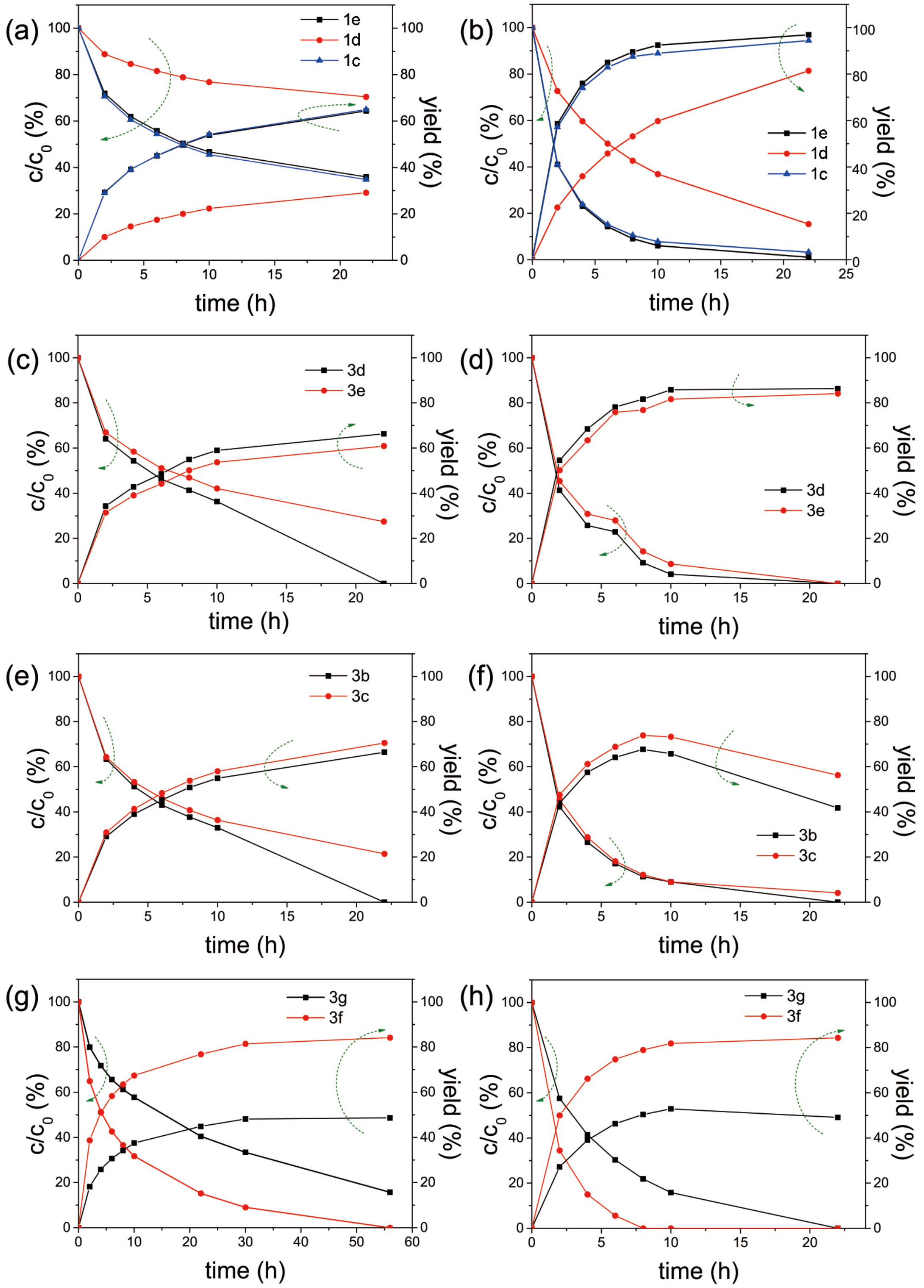


Fig. S7 Competitive reactions of substrates with different substituent position. (a) The substrates were 0.03 mmol 1-bromo-2-chlorobenzene (**1e**), 0.03 mmol 1-bromo-3-chlorobenzene (**1d**), and 0.03 mmol 1-bromo-4-chlorobenzene (**1c**). (b) The substrates were 0.01 mmol 1-bromo-2-chlorobenzene (**1e**), 0.01 mmol 1-bromo-3-chlorobenzene (**1d**), and 0.01 mmol 1-bromo-4-chlorobenzene (**1c**). (c) The substrates were 0.03 mmol 1-bromonaphthalene (**3f**) and 0.03 mmol 2-bromonaphthalene (**3g**). (d) The substrates were 0.015 mmol 1-bromonaphthalene (**3f**) and 0.015 mmol 2-

bromonaphthalene (**3g**). (e) The substrates were 0.03 mmol 2-bromothiophene (**3b**) and 0.03 mmol 3-bromothiophene (**3c**). (f) The substrates were 0.015 mmol 2-bromothiophene (**3b**) and 0.015 mmol 3-bromothiophene (**3c**). (g) The substrates were 0.03 mmol 4-bromoquinoline (**3e**) and 0.03 mmol 6-bromoquinoline (**3d**). (h) The substrates were 0.015 mmol 4-bromoquinoline (**3e**) and 0.015 mmol 6-bromoquinoline (**3d**). The reaction conditions were same as typical procedure mentioned above.

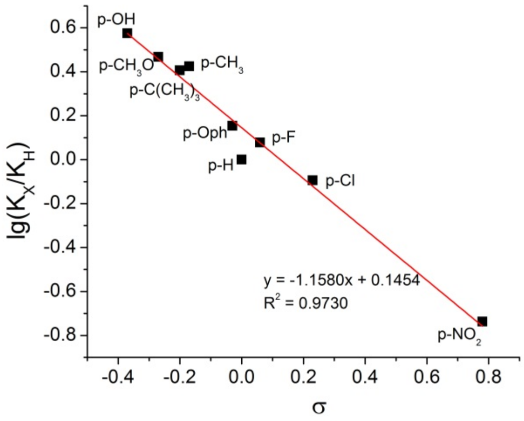


Fig. S8 Hammett plot for the aryl bromide-chloride exchange reactions photocatalyzed by $FeCl_3$. The reaction conditions were same as typical procedure in Table 1. All the selected substrates have good selectivities for the chlorinated products at the initial reaction stage at least.

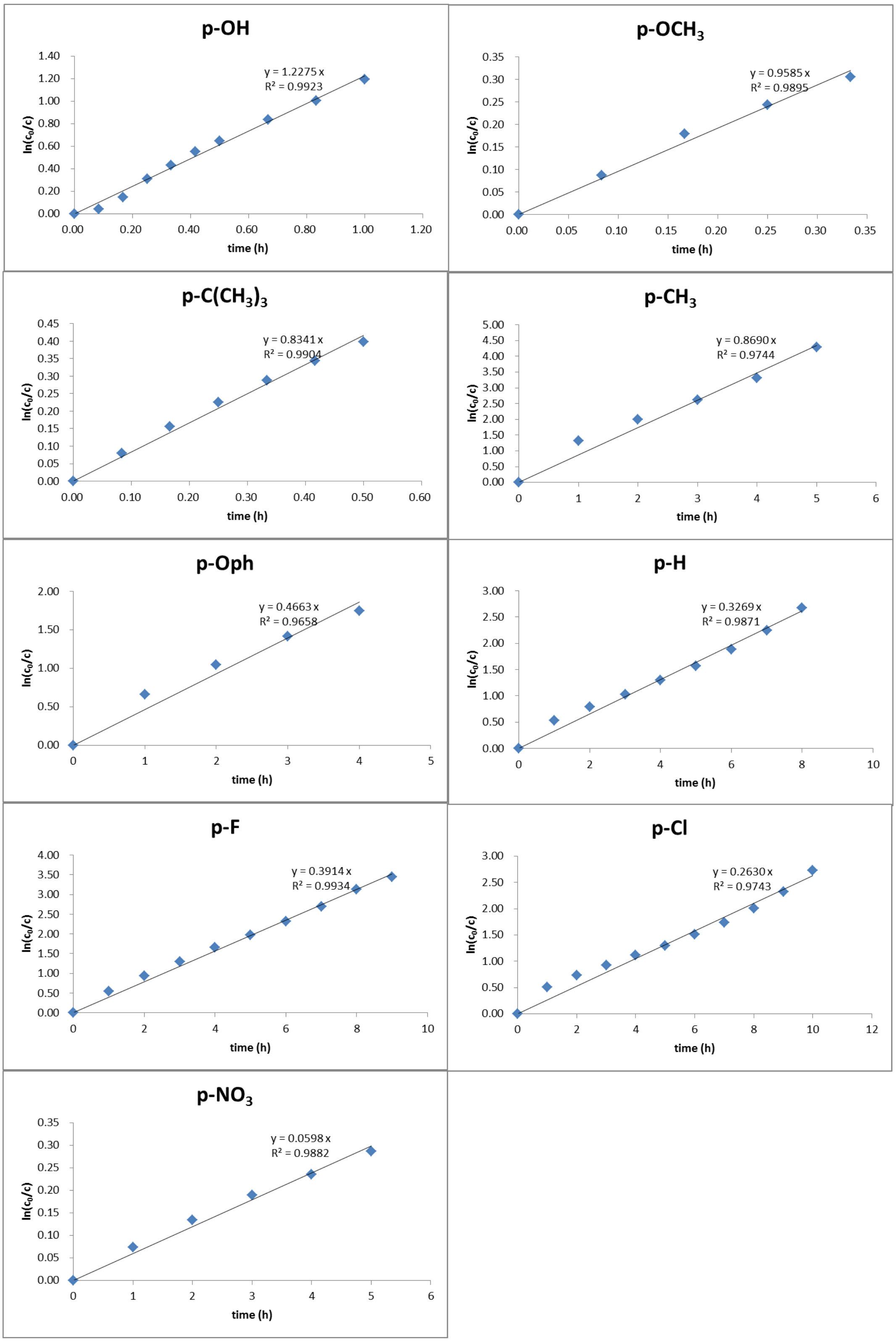


Fig. S9 The fitting of rate constant (k) for bromobenzenes with different p-substituents in the aryl bromide-chloride exchange reactions. The reaction conditions were same as typical procedure mentioned above.

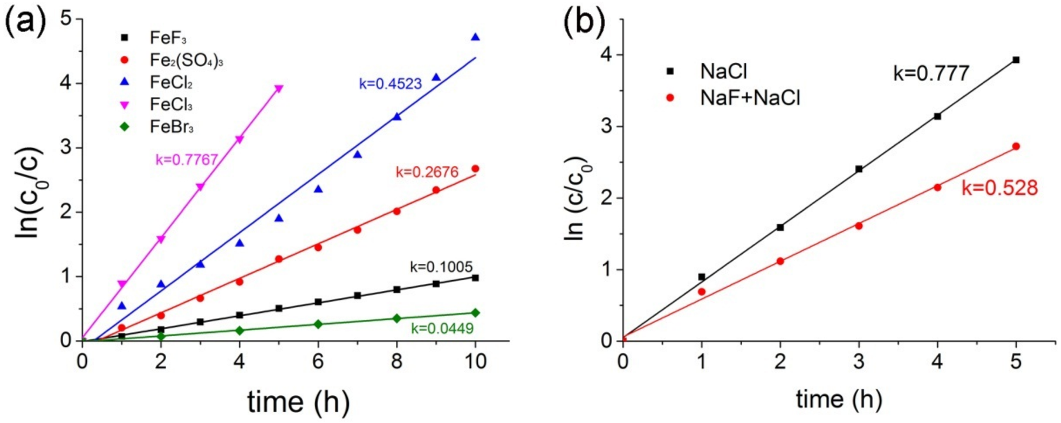


Fig. S10 (a) The catalytic effects of different iron salts. Reaction conditions: 1.0 mM bromobenzene, 5.0 equiv. NaCl and 0.5 mM iron salt in 30 mL of acetonitrile, under irradiation with UV light (λ>360 nm). (b) Effect of F^- on the reaction rate. Reaction conditions: 1.0 mM bromobenzene, 0.5 mM $FeCl_3$ (purity: 98%) in 30 mL of acetonitrile, excessive addition of NaCl with or without NaF under irradiation with UV light (λ>360 nm).

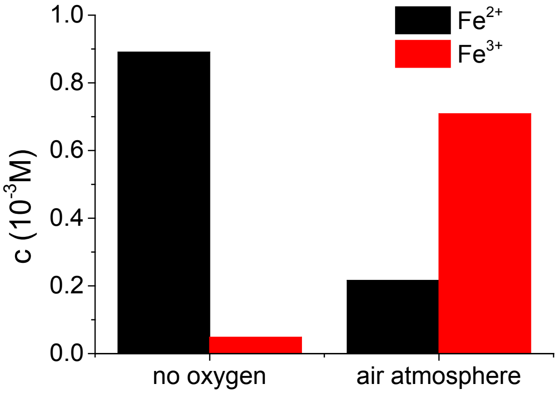


Fig. S11 The transformation of Fe(III) and Fe(II) in $FeCl_2$ solution after exposure in air. The detective method was described in experimental section. The valence of Fe was changed dramatically and measured in two minutes after exposure in air with continuous stirring. The content of Fe(III) was obtained by subtracting content of Fe(II) from the total amount of iron ion.

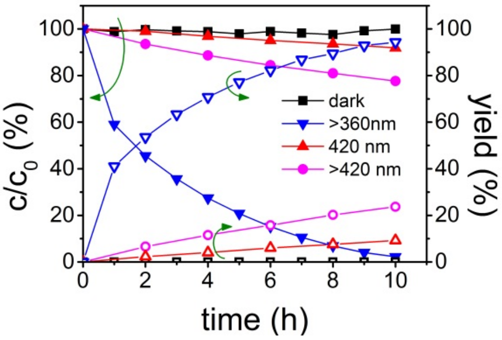


Fig. S12 The catalytic effects under irradiations of different wavelength.