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Research Note

Cuprous cluster as effective single-molecule metallaphotocatalyst in white light-driven C—H arylation



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1. Introduction

ABSTRACT

This study investigated a series of ferrocenyltelluroether based cuprous halide clusters as effective singlemolecule metallaphotocatalysts (SMP) in white light-driven C—H arylation at room temperature and air. A systematic mechanistic study reveals that Cu(1) cluster can be irradiated by visible light to promote proton-coupled electron transfer (PCET), during which the electron from Cu(1)* leaves together with the proton from benzothiazole C—H, leading to the formation of benzothiazolate-coordinated Cu(11) intermediate and aryl radical. Subsequently, the electron transfer (ET) from the ferrocene unit to the Cu(II) center releases the reactive benzothiazolate to form the target product with aryl radical. The advantages of these copper(1) halide clusters as SMP include high photocatalytic efficiency, structure adjustability, mild reaction conditions and good functional group tolerance.

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Enormous efforts have been paid to efficient C—H arylation due to its significance in chemical synthesis, pharmaceutics and material fields [1–4]. To develop novel, economical and highly efficient strategies for different types of C—H arylation under mild conditions remains a very challenging subject. One approach that has received much attention recently is the synergistic combination of transition metal catalysis and photocatalysis, termed metallaphotocatalysis (MP). In MP platform, with suitable light irradiation, photocatalyst can produce powerful driving force, which effectively activates transition metal catalysts for direct coupling of non-traditional nucleophile partners. The MP platform can perform well under the milder reaction conditions, with the advantages such as visible-light irradiation, air, absence of high temperature and external strong oxidants (Fig. 1) [5–10].

The Pd \cdots Ru MP platform for C—H arylation with visible light at room temperature was first reported by Sanford in 2011 [11]. Ackermann accomplished the photoinduced C—H arylation with

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Cu…Ir MP [12–15]. Incorporating the hydrogen atom transfer (HAT) mode with Ni...Ir MP, MacMillan developed a ternary catalytic system that enables the selective arylation of sp³ C–H bonds [16]. Doyle reported that halogen radicals can function as HAT reagents for Ni…Ir MP-mediated α oxy C—H arylation [17]. Lee found Au...Ru MP conferred regioselectivity via the crucial Aucatalyzed C-H activation step [18]. In all these aforementioned dual MP systems, the excited state of the photocatalysts must live long enough to encounter transition metal catalysts and/or substrates before undergoing deactivation. So the expensive ruthenium or iridium complexes, are pre-requisite photocatalysts due to their strong absorption in visible light region and sufficient long excited state lifetimes. The quest to culminate atom-economical photocatalytic methods is then the driving force to explore SMP, which bears 'double duty' in harvesting visible light and enabling catalysis via unimolecular. As an emerging area, to construct effective visible light promoted SMPs in C-H arylation and to elucidate the operative mode of activation will provide strong support to the development of valuable transformations of organic molecules.

Copper complexes in catalytic processes have been actively explored owing to their diverse structures with oriented electron transfer properties and rich photoexcited states [19–22]. Recently, Peters has achieved the N–C, S–C, O–C and C–C coupling of





Fig. 1. Light-driven C—H arylation with MP and SMP (Het = Heterocycle).

heterocycle with organic halides under blue light irradiation and mild conditions, in which, the *in situ* generated copper complex was proposed as photocatalyst [23–25]. Hwang reported that Sonogashira reaction can operate under irradiation of visible light with low loading of CuCl catalysts [26]. Due to the adjustable compositions and designable architecture networks, copper-based coordination polymers have been developed as a new member of photocatalytic materials. Song demonstrated that the nanobelt of air-stable copper-phenylacetylide coordination polymer can be used in effective elimination of organic pollutants under visible light irradiation [27]. Overall, polynuclear copper(I) halide clusters (Cu_nX_n) have shown great potential application in the luminescence and catalysis field [28-30]. Considering the fact that stable copper(I) complexes can be constructed with soft Se or Te donor atoms, our group has embarked on the systematic study of Cu_nX_n clusters based upon neutral ferrocenylchalcogenoethers, FcCu_nX_n (Fc = ferrocenyl) [31,32]. In the previous study, we found that these FcCu_nX_n showed excellent catalytic activities in C-N coupling reaction of imidazole with iodobenzene under mild condition [31,32]. A concerted PCET process from the Cu(I) center and substrate facilitates the formation of Cu(II) intermediate. The different coordination mode of Cu(I)/Cu(II), together with the redox ferrocene unit, lead to the formation of the target product. Furthermore, we successfully constructed the core-shell $TiO_2@[Cu_2I_2L_2]_n$ material which shows an effective visible-light photocatalytic property in the reduction of aqueous chromium(VI) [33]. The excited $[Cu_2I_2L_2]_n$ under visible light illumination generated electrons, which can be transferred into the conduction band of TiO₂ for the reduction of chromium (VI) species. With these in mind, combining the progress in C-H activation with copper-containing catalysts, we are now exploring a protocol for visible light-mediated C-H arylation using $FcCu_nX_n$ clusters as the possible SMP candidates (Fig. 1).



Scheme 1. Molecular structures of clusters 1-8.

2. Materials and methods

2.1. Reagents

Ferrocene, tellurium, dibromopropane, α, α' -dibromo-*p*-xylene, α, α' -dibromo-*m*-xylene, benzothiazole, benzoxazole, iodobenzene, 1-iodo-4-methylbenzene, 1-iodo-4-methoxybenzene, 1-iodo-4-chlorobenzene, 1-iodo-4-(trifluoromethyl)benzene, 1-iodo-3-methylbenzene, 1-iodo-3-methoxybenzene, 1-iodo-3-chlorobenzene, 1-iodo-3-(trifluoromethyl)benzene, 1ithium *tert*-butoxide and CuX (X = Br or I) are of AR grade. Copper clusters **1–8** were prepared according to our reported methods [31,32]. All solvents used were purified following standard procedures prior to use.

2.2. Characterization

¹H NMR spectra were recorded on a Bruker DRX spectrometer (400 MHz) at ambient temperature and the chemical shifts were referenced to the solvent signal in CDCl₃. X-ray photoelectron spectroscopy (XPS) with PHI 5000 VersaProbe of UIVAC-PHI and all binding energies were referenced to the C1s peak at 284.8 eV. The solution electron paramagnetic resonance (EPR) spectrum was obtained using Bruker EMX plus-6/1 X-band variable-temperature apparatus. Fourier transform infrared spectroscopy (FTIR) was recorded within the 400–4000 cm⁻¹ region on a Thermo Scientific Nicolet IS10 FTIR spectrometer using KBr pellets. UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded using

Table 1

Model photo-assisted C-H arylation using copper clusters 1-8.^a



Entry	Catalyst	Solvent	Yield [%] ^b
1	1	DMSO	86
2	2	DMSO	61
3	3	DMSO	63
4	4	DMSO	73
5	5	DMSO	60
6	6	DMSO	70
7	7	DMSO	64
8	8	DMSO	40
9	1	THF	42
10	1	H ₂ O	trace
11	1	MeCN	59
12	1	Et ₂ O	23
13	1	DMF	70
14	CuI (20% mol) + free ligand in 1°	DMSO	56
15	CuI (20% mol)	DMSO	0
16	None	DMSO	0
17	1 (dark)	DMSO	0
18	1	DMSO	52 ^d

^a Model reaction condition: iodobenzene (1.25 mmol), benzothiazole (0.25 mmol), copper cluster (20 mol% Cu), t-BuOLi (0.75 mmol), solvent (2.0 mL).

^b Isolated yield of target product.

^c Free ligand in **1** is diferrocenyl ditelluride.

^d Only changing the ratio of substrates: iodobenzene (0.25 mmol), benzothiazole (0.25 mmol).



Scheme 2. The scopes of azole and iodobenzene in the C–H arylation with model reaction condition: iodobenzene (1.25 mmol), azole (0.25 mmol), cluster 1 (20 mol% Cu), t-BuOLi (0.75 mmol), DMSO (2.0 mL).

PerkinElmer Lambda 950 UV/Vis/NIR Spectrophotometer, with BaSO₄ as the reference. UV–vis absorption spectra were measured with Hitachi spectrophotometer UV-3900. Steady state photoluminescence emission spectra were measured with Horiba Jobin Yvon FluoroMax-4 and the fluorescence photos of samples were taken with Hitachi fluorescence spectrophotometer F-7000. Fluorescence

decay and time-resolved emission spectra were recorded using an Edinburgh FLSP920 fluorescence spectrophotometer equipped with tunable bonds of laser from 400 nm to 500 nm. GC experiments were performed on an Agilent 7890B gas chromatograph equipped with a 30 m \times 0.32 mm \times 0.25 μ m HP-5 capillary column and a FID detector.



Fig. 2. Proposed mechanism.



Fig. 3. (a) UV-Vis spectra of 1 and 1i suspension in DMSO solution; (b) UV-vis DRS spectra of solid 1 and 1i.

2.3. Evaluation of catalytic activity

All reagents were weighed and handled in air at room temperature. For the studies of catalytic activity reactions, a White-LED with the power density of 300 mW/cm², was employed as the light source. A general procedure: heterocycle substrate (0.25 mmol), aryl halide (1.25 mmol), copper(I) cluster (20 mol%), *t*-BuOLi (0.75 mmol), and DMSO (2.0 mL) were placed in a pre-dried 10 mL quartz tube. The tube was opened to air and the resulting reaction mixture was stirred for 16 h under white light irradiation at ambient temperature. Next, the crude reaction mixture was diluted with 20 mL H₂O and extracted with 3 × 20 mL EtOAc. The solvent of the combined organic phases was removed under reduced pressure. The resulting residue was purified by preparative TLC (EtOAc:n-hexane = 1:20 (v/v)) to afford the desired product.

3. Results and discussion

3.1. Investigation of initial optimization and substrate scopes

We initiated the catalytic studies by probing the photo-assisted C—H arylation of benzothiazole with iodobenzene. Eight ferrocenyltelluroethers $FcCu_nX_n$, **1–8** (Scheme 1), were chosen for the screening as SMP candidates. The model reactions were performed using copper cluster with 20 mol% Cu as the SMP, 5 equiv. of iodobenzene and 3 equiv. of base relative to the amount of



Fig. 4. XPS spectra of (a) 1 and 1i; (b) Cu2p in 1; (c) Cu2p in 1i; (d) Te3d in 1 and 1i; (e) S2p in 1i; and (f) N1s in 1i.



Fig. 5. (a) Fluorescence spectra of 1 and 1i in DMSO excited at 459 nm; (b) Fluorescence lifetime decay profiles of fluorescence emission bands of 1, and 1i excited in the region of 400–500 nm.

benzothiazole at room temperature, air and DMSO solvent. Product N-(4-phenyl)benzothiazole in isolated yield was shown in Table 1. While different SMPs provided comparable results (Table 1, entries 1-8), the best performance was obtained with cluster 1 which gave the target product in 86% yield. A reaction conducted in other reaction media, including THF, H₂O, MeCN, Et₂O and DMF, proceeded less efficiently (Table 1, entries 9-13). The catalytic activity of CuI and free ligand diferrocenyl ditelluride (Table 1, entry 14) was much worse than that of cluster 1, and no product was observed if only CuI was used (Table 1, entry 15). The C-H arylation did not occur in the absence of SMP or in the dark (Table 1, entries 16 and 17). Changing the molar ratio of iodobenzene and benzothiazole to 1:1, the target product is obtained in lower yield (52%) (Table 1, entry 18) than that using 5 equiv. of iodobenzene (86%) (Table 1, entry 1). The scopes of the substrates in the photo-assisted C-H arvlation were then explored by probing different substituted azole to react with iodobenzene (Scheme 2). Cluster 1 was proved to have good functional group tolerance to deliver the desired C–H arylation products (Figs. S1–S11).

3.2. Mechanism study

As shown in Fig. 2, the proposed mechanism includes five steps: (i) Cu(I) center is irradiated by visible light to obtain the excited state Cu(I)*; (ii) The photo promoted PCET is then progressed [34–37], in which the electron from Cu(I)* coupling the proton from benzothiazole C—H leads to penta-coordinated Cu(II) complex with two I[–], two Te atoms and one benzothiazolate. H⁺ is consumed by *t*-BuOLi, and electron transferred to aryl halide giving aryl radical and I[–]; (iii) The ET from Fc unit to the Cu(II) gives ferrocenium unit (Fc⁺, the oxidized form of ferrocene) and Cu(I); (iv) The released reactive benzothiazolate combines aryl radical to form the product; (v) Finally the Fc⁺ was reduced by I[–] to produce the neutral Fc.

The proposed mechanism is supported by a series of experiments. Firstly, UV-vis spectrum of cluster **1** in DMSO exhibited two absorption bands at 394 nm ($\varepsilon = 5.30 \times 10^7 \text{ M}^{-1} \text{ m}^{-1}$) and 465 nm ($\varepsilon = 3.74 \times 10^7 \text{ M}^{-1} \text{ m}^{-1}$), which nicely overlap with the emission band of the white light used for the catalytic reactions (Fig. 3a). It was found that when benzothiazole and *t*-BuOLi were added into the solution of **1**, a yellow green mixture appeared under white light, which can be ascribed to the formation of the Fc⁺. Diethyl ether was then added into solution to precipitate the intermediate product, **1i**. In the UV-vis DRS spectra of **1** and **1i** (Fig. 3b), the strong and broad visible absorption band in the region of 380–650 nm suggests that **1** can behave as efficient photocatalyst candidate in visible light-driven reaction. This is in accordance with the result that the catalytic activity of CuI and free ligand (Table 1, entry 14) was much worse than that of cluster **1**.

Secondly, X-ray photoelectron spectra (XPS) in Fig. 4 indicates the coexistence of Cu(I) and Cu(II) in 1i. The main peak of Cu $2p_{3/2}$ at 933.0 eV and the satellite peak at 942.5 eV in **1i** verify that most of Cu centers are in +2 state (Fig. 4a-c). The weak peak at 931.7 eV and the ratio of intensity of the satellite peak to that of the main peak ($I_{sat}/I_{main} = 0.77$) in **1i** can be ascribed to the existence of Cu(I) [38,39]. When a solution of **1**, benzothiazole and *t*-BuOLi is irradiated under the model condition by visible light at room temperature, a weak EPR signal is observed which can be tentatively ascribed to the Cu(II) in 1i (Fig. S12) [25]. The XPS bands of Te 3d, S 2p and N 1 s shown in Fig. 4d-f, respectively, supports the coordination of benzothiazolate to Cu center in 1i, which was also confirmed by FTIR (Fig. S13). The v_{C-H} peak of free benzothiazolate at 3030–3020 cm⁻¹ disappeared in the FTIR spectrum of **1i**. Moreover, the $v_{C=N}$ (1600–1300 cm⁻¹) and v_{C-S} (780– 600 cm⁻¹) of benzothiazolate are also shifted significantly due to the formation of the intermediate 1i (Fig. S13).

Thirdly, the steady-state photoluminescence emission spectrum of cluster **1** under 459 nm excitation (Fig. 5a) revealed a weak band at 535 nm, the obvious quenching effect can be ascribed to the photoinduced electron transfer (PET) process from the ferrocene moiety to the excited copper center. And for **1i**, the intensity of photoluminescence increased significantly, indicating that



Scheme 3. Probing a radical mechanism.

the PET process is prohibited due to the ferrocenium unit Fc⁺ (Fig. 5a). Then the excited-state quenching kinetics of 1 and 1i was further investigated (Fig. 5b). A clear biexponential decay of the emission was observed, which gives a lifetime of 3.1 ns (64%) and 0.6 ns (36%) for 1, 1.8 ns (60%) and 0.2 ns (40%) for 1i, respectively (Fig. 5b) [40]. These differences may be due to the structure variation of the Cu cluster and the potential change of the oxidation state of Fe in the ferrocene unit. The longer fluorescence lifetime separation process can be attributed to the intrinsic fluorescence lifetime of metal cluster, while the short lifetime component suggests the presence of the quenched fluorescence of cluster center [41]. As compared to the penta-coordinate mode of Cu (II) in **1i**, the more stable tetrahedral coordination geometry of Cu(I) in **1** can protect the Cu(I) center in excited state, and elongate the emission lifetime. Similar phenomena have been observed before [42].

Fourthly, the addition of the radical TEMPO into the catalytic system resulted in a significant inhibition of the catalytic performance of **1** (Scheme 3a). When 1 equiv. of TEMPO (compared to the benzothiazole) was applied, only 32% yield of the target product was obtained, whereas under the same conditions the target product was 86% yield without TEMPO. When 2 equiv. of TEMPO (compared to the benzothiazole) was used, the SMP performance of the cluster **1** is completely inhibited because no product can be detected after the reaction. This phenomenon can be ascribed to a rapid reversible PCET process between TEMPO and TEMPOH (Scheme 3b), in agreement with previous observations [43].

Finally, in our proposed mechanism, the photo-promoted PCET is the prerequisite step for the generation of aryl radical. So the application of iodobenzene in excess is essentially important. In a control experiment using benzothiazole and iodobenzene in 1:1 molar ratio, the target product was obtained in much lower yield of only 52% compared to 86% that using 5 equiv. of iodobenzene (Table 1, entry 18 vs entry 1). And no biphenyl compound was obtained as byproduct (Fig. S14). This indicates that once the benzothiazole is consumed, no aryl radical can then be generated effectively. Due to short lifetime of aryl radicals, excess iodobenzene can effectively obtain electron from PCET step to form aryl radical, then improve the yield of the target product.

4. Conclusions

In summary, the ferrocenyltelluroether based copper(I) halide clusters have been proven to be the effective SMP in white lightdriven C–H arylation of azoles. The 'double duty' of the copper(I) halide clusters enables the success: (I) Ferrocenyltelluroether based copper(I) cluster owns high visible-light activity; (II) Copper(I) acts as high catalytic-active participant in the forming step of Cu-benzothiazolate intermediate. In this catalytic cycle, PCET process avoids the high-energy intermediate state, and redox ferrocene unit plays the important role of electron shuttle to stabilize the intermediate redox products. These synergistic effects endow ferrocenyltelluroether based copper(I) halide clusters with SMP feature to activate the corresponding inert substrates. The present visible-light-driven photocatalytic system opens new opportunities for C-H bond activation. Future directions of this field are to construct cost-effective and more environment-friendly chemical transformations based on recyclable SMP platforms.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.08.017.

References

- [1] I.V. Seregin, V. Gevorgyan, Chem. Soc. Rev. 36 (2007) 1173–1193.
- [2] O. Daugulis, H.Q. Do, D. Shabashov, Acc. Chem. Res. 42 (2009) 1074-1086.
- [3] J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, Chem. Soc. Rev. 40 (2011) 4740– 4761.
- [4] P. Nareddy, F. Jordan, M. Szostak, ACS Catal. 7 (2017) 5721–5745.
- [5] C.K. Prier, D.A. Rankic, D.W.C. MacMillan, Chem. Rev. 113 (2013) 5322-5363.
 [6] M.N. Hopkinson, B. Sahoo, J.-L. Li, F. Glorius, Chem. Eur. J. 20 (2014) 3874-3886.
- [7] K.L. Skubi, T.R. Blum, T.P. Yoon, Chem. Rev. 116 (2016) 10035–10074.
- [8] L. Huang, M. Rudolph, F. Rominger, A.S. Hashmi, Angew. Chem. Int. Ed. 55 (2016) 4808–4813.
- [9] J. Twilton, C. Le, P. Zhang, M.H. Shaw, R.W. Evans, D.W.C. MacMillan, Nat. Rev. Chem. 1 (2017) 0052.
- [10] V. Gevorgyan, M. Ratushnyy, M. Parasram, Y. Wang, Angew. Chem. Int. Ed. 57 (2018) 2712–2715.
- [11] D. Kalyani, K.B. McMurtrey, S.R. Neufeldt, M.S. Sanford, J. Am. Chem. Soc. 133 (2011) 18566–18569.
- [12] F. Yang, J. Koeller, L. Ackermann, Angew. Chem. Int. Ed. 55 (2016) 4759–4762.
- [13] P. Gandeepan, J. Koeller, L. Ackermann, ACS Catal. 7 (2017) 1030–1034.
- [14] P. Gandeepan, J. Mo, L. Ackermann, Chem. Commun. 53 (2017) 5906–5909.
- M.M. Lorion, K. Maindan, A.R. Kapdi, L. Ackermann, Chem. Soc. Rev. 46 (2017) 7399–7420.
 M.M. Shawi V.W. Shurtleff, J.A. Terrett, J.D. Cuthbarteen, D.W.C. MacMillan
- [16] M.H. Shaw, V.W. Shurtleff, J.A. Terrett, J.D. Cuthbertson, D.W.C. MacMillan, Science 352 (2016) 1304–1308.
- [17] B.J. Shields, A.G. Doyle, J. Am. Chem. Soc. 138 (2016) 12719-12722.
- [18] V. Gauchot, D.R. Sutherland, A.-L. Lee, Chem. Sci. 8 (2017) 2885–2889.
- [19] G. Evano, N. Blanchard, M. Toumi, Chem. Rev. 108 (2008) 3054-3131.
- [20] A.J. Hickman, M.S. Sanford, Nature 484 (2012) 177–185.
- [21] X.-X. Guo, D.-W. Gu, Z.-X. Wu, W.-B. Zhang, Chem. Rev. 115 (2014) 1622–1651.
- [22] S. Paria, O. Reiser, ChemCatChem 6 (2014) 2477–2483.
- [23] J. He, C.-Y. Chen, G.C. Fu, J.C. Peters, ACS Catal. 8 (2018) 11741-11748.
- [24] W. Zhao, R.P. Wurz, J.C. Peters, G.C. Fu, J. Am. Chem. Soc. 139 (2017) 12153– 12156.
- [25] J.M. Ahn, T.S. Ratani, K.I. Hannoun, G.C. Fu, J.C. Peters, J. Am. Chem. Soc. 139 (2017) 12716–12723.
- [26] A. Sagadevan, K.C. Hwang, Adv. Synth. Catal. 354 (2012) 3421-3427.
- [27] H.-Y. Jiang, P. Zhou, Y.-Y. Wang, R. Duan, C.-C. Chen, W.-J. Song, J.-C. Zhao, Adv. Mater. 28 (2016) 9776–9781.
- [28] W. Liu, K. Zhu, S.J. Teat, G. Dey, Z.-Q. Shen, L. Wang, D.M. O'Carroll, J. Li, J. Am. Chem. Soc. 139 (2017) 9281–9290.
- [29] D.-Y. Shi, R. Zheng, M.-J. Sun, X.-R. Cao, C.-X. Sun, C.-J. Cui, C.-S. Liu, J.-W. Zhao, M. Du, Angew. Chem. Int. Ed. 56 (2017) 14637–14641.
- [30] B. Huitorel, H. El Moll, R. Utrera-Melero, M. Cordier, A. Fargues, A. Garcia, F. Massuyeau, C. Martineau-Corcos, F. Fayon, A. Rakhmatullin, S. Kahlal, J.Y. Saillard, T. Gacoin, S. Perruchas, Inorg. Chem. 57 (2018) 4328–4339.
- [31] W. Ji, J. Qu, S. Jing, D.-R. Zhu, W. Huang, Dalton Trans. 45 (2016) 1016–1024.
- [32] C.-A. Li, W. Ji, J. Qu, S. Jing, F. Gao, D.-R. Zhu, Dalton Trans. 47 (2018) 7463– 7470.
- [33] W. Ji, J. Qu, C.-A. Li, J.-W. Wu, S. Jing, F. Gao, Y.-N. Lv, C. Liu, D.-R. Zhu, X.-M. Ren, W. Huang, Appl. Catal. B: Environ. 205 (2017) 368–375.
- [34] C.R. Waidmann, A.J.M. Miller, C.-W.A. Ng, M.L. Scheuermann, T.R. Porter, T.A. Tronic, J.M. Mayer, Energy Environ. Sci. 5 (2012) 7771–7780.
- [35] O.S. Wenger, Acc. Chem. Res. 46 (2013) 1517-1526.
- [36] S. Hammes-Schiffer, J. Am. Chem. Soc. 137 (2015) 8860-8871.
- [37] J.C. Lennox, D.A. Kurtz, T. Huang, J.L. Dempsey, ACS Energy Lett. 2 (2017) 1246– 1256.
- [38] C.-J. Tang, J.-F. Sun, X.-J. Yao, Y. Cao, L.-C. Liu, C.-Y. Ge, F. Gao, L. Dong, Appl. Catal. B: Environ. 146 (2014) 201–212.
- [39] X.-J. Yao, L. Zhang, L.-L. Li, L.-C. Liu, Y. Cao, X. Dong, F. Gao, Y. Deng, C.-J. Tang, Z. Chen, L. Dong, Y. Chen, Appl. Catal. B: Environ. 150–151 (2014) 315–329.
- [40] X.-Y. Wu, W.-T. Wu, X.-N. Cui, J.-Z. Zhao, M.-B. Wu, J. Mater. Chem. C 4 (2016) 2843–2853.
- [41] J. Qu, Q. Xia, W. Ji, S. Jing, D.-R. Zhu, L. Li, L. Huang, Z.-F. An, C.-Q. Xin, Y. Ni, M.-X. Li, J.-D. Jia, Y.-L. Song, W. Huang, Dalton Trans. 47 (2018) 1479–1487.
- [42] M.W. Mara, K.A. Fransted, L.X. Chen, Coordin. Chem. Rev. 282–283 (2015) 2–
- [43] A. Badalyan, S.S. Stahl, Nature 535 (2016) 406-410.