

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: W. Wu, Y. Wong, Z. Tan and J. Wu, *Catal. Sci. Technol.*, 2018, DOI: 10.1039/C8CY01240G.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/catalysis

Published on 24 July 2018. Downloaded by University of Sussex on 7/25/2018 12:05:06 PM

YAL SOCIETY CHEMISTRY

Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Photo-Induced Thiol Coupling and C–H Activation Using Nanocrystalline Lead-Halide Perovskite Catalysts

Wen-Bin Wu,^{a‡} Ying-Chieh Wong,^{a‡} Zhi-Kuang Tan,^{*ab} Jie Wu^{*a}

The use of photon energy to promote chemical transformations offers versatile control of reaction kinetics and progress. Over the past decade, many photoactive transition-metal complexes and organic chromophores were developed to catalyze chemical transformations, enabling a myriad of reactions and compounds that were previously inaccessible via traditional synthetic methods. Here, we demonstrate the photocatalytic oxidative coupling of organic thiols using cesium lead halide perovskite nanocrystals as photocatalysts. The photo-catalyzed thiol coupling reactions selectively produced symmetric and unsymmetrical disulfides in high yields (68-96% isolated yields). Additionally, we discovered a perovskite-catalyzed phosphonylation of tertiary amines via visible-light-mediated cross-dehydrogenative coupling reaction, and obtained good isolated yields (50-96%). The variety of visible-light-induced photocatalytic processes that perovskite nanocrystals are capable of, coupled with their facile preparation, easily tunable redox potentials, high catalytic efficiency and reusability, presents great opportunities for their future applications in green and sustainable organic synthesis.

1. Introduction

Visible-light-mediated photochemistry has witnessed dramatic developments over the past ten years.¹⁻⁶ Because most organic substrates do not absorb photons in the visible-light region, using visible-light rather than strong UV light to promote organic transformations often delivers a cleaner and more selective reaction. More importantly, by activation with visible-light, the photocatalyst can function as a single-electron redox mediator or facilitate energy transfer to activate a diverse range of organic substrates, which enables previously inaccessible transformations and products. In this context, transition-metal chromophores such as Ru and Ir polypyridyl complexes have garnered particular recognition due to their rich redox chemistry at the MLCT (metal-toligand charge-transfer) excited states.⁴ On the other hand, organic photocatalysts enable unique chemistry far more than just "metalfree" alternatives to transition-metal photocatalysts.¹ Among other possible photocatalysts, inorganic semiconductors, such as quantum dots (QDs) and TiO₂, offer a unique way to harvest light energy and activate organic molecules through electron-holetransfer. Notably, in 2014, the Wu group reported the use of CdSe QDs as the photocatalyst to achieve an oxidant-free dehydrogenative coupling of thiols to symmetric disulfides in very

‡ These authors contributed equally to this work.

high efficiency.⁷ The Xu and Xiao group discovered that Ni-modified CdS nanoparticles could efficiently catalyze an aerobic oxidation of alcohols to aldehydes and ketones.⁸ Very recently, the Weix group demonstrated that the CdSe QDs could serve as an advantageous replacement for Ru- or Ir-based photoredox catalysts with improved turnover numbers.⁹ Furthermore, the König group has described that the appropriate combination of heterogeneous semiconductors with chiral organocatalysts could promote highly stereoselective transformations under visible-light-irradiation.¹⁰ However, development of semiconductors as photocatalysts for organic bond formation is still at its early stage,⁷⁻²¹ and there remains a critical need for the development of effective heterogeneous photocatalysts to enable valuable and sustainable synthetic processes.

Lead halide perovskites, such as CsPbX₃ and CH₃NH₃PbX₃ (X represents I, Br or Cl, Fig. 1a), exhibit exceptional semiconductor properties,²²⁻²⁴ and have been leveraged in various optoelectronic applications such as photovoltaics²⁵⁻³⁰ and light-emitting devices.³¹⁻ Compared to other semiconductors, perovskites offer easy materials preparation and application via low-temperature solution-based methods, and allow facile tuning of their semiconductor bandgap through the control of their halide compositions. Fig. 1a shows the unit cell crystal structure of perovskites and their electronic bandgaps. A change in the halide content from iodide to bromide to chloride allows the bandgap to be tailored from 1.8 eV to 3.0 eV, as estimated from the absorbance and photoluminescence (PL) spectra of the respective perovskites in Fig. 1b. Perovskites, being direct-bandgap semiconductors, possess high extinction coefficient, and depending on their halide content, could allow light absorption over a wide UV to near infrared range. Hence, we envision that the solution-dispersible nanocrystals (NC) of CsPbX₃ perovskites,³⁷ which exhibit high photo-activity and large

^{a.} Department of Chemistry, National University of Singapore, 3 Science Drive 3, S117543, Singapore.

^{b.} Solar Energy Research Institute of Singapore, National University of Singapore, 7 Engineering Drive 1, S117574, Singapore.

 $^{^{+}}$ Electronic Supplementary Information (ESI) available: Detailed experimental procedures, spectral data for all compounds, time tracking studies, light "On-Off" study, reusability test, quantum yield determination, H_2 detection, and proposed mechanism. See DOI: 10.1039/x0xx00000x

surface area, will be a promising class of photocatalysts.³⁸ To the best of our knowledge, there has been no reports on the use of lead halide perovskites as photocatalysts to synthesize useful organic molecules. We herein



Fig 1. (a) Unit cell structure and energy level diagram of CsPbX₃ perovskites. Energy levels were estimated from literature values, ³⁹⁻⁴⁰ and converted to redox potentials vs. SCE (-4.68 eV vs. vacuum). (b) Absorbance (dashed lines) and photoluminescence (solid lines) spectra of perovskites.

report that $CsPbX_3$ perovskites can effectively activate S–H and C–H bonds under visible-light-irradiation for subsequent transformations.

2. Results and Discussion

2.1 CsPbX₃ catalyzed oxidative coupling of thiols to disulfides

Disulfides are essential for proteins to fold into biologically active conformations,⁴¹⁻⁴² and were also widely applied in fine chemical industry as anti-oxidants, pharmaceuticals, pesticides, and as vulcanization agents.⁴³ Symmetric disulfides are normally accessed by oxidative coupling of thiols with oxidants, which normally suffer from at least one drawback such as over-oxidation, high catalyst-loading, excess and expensive oxidants, strong acidic or basic media, and high temperature.⁴⁴ The development of a mild, green, selective, and efficient thiol coupling protocol is still highly desired. In this context, photocatalysis offers a milder pathway to achieve this important transformation.^{7, 45-47}

Our investigation commenced with using thiophenol **1a** as the substrate and a broadband white light-emitting diode (LED, 420 nm to 700 nm emission, Fig. 1b) as light source to investigate the effect of various parameters on the photo-coupling reaction. As shown in Table **1**, we discovered that thiophenol **1a** can be successfully coupled to disulfide **2a** in virtually quantitative yield in CH_2CI_2 by

using a 1 mol% CsPbBr₃ perovskite catalyst (entry 1). No external oxidant was required, as a significant amount of product **2a** was generated under strict oxygen-free environment (entry 2), with molecular hydrogen produced as the reduction by-product (Fig. **Table 1** Condition optimization for CsPbBr₃ perovskite catalyzed disulfide formation^{*a*}

2 X 🌘	SH CsPbBr ₃ (1 mol%) CH ₂ Cl ₂ , white LEDs, rt, air, 6 h	S'S
	1a	2a
Entry	Deviation from the standard condition	Yield of 2a (%) ^b
1	none	98
2	oxygen-free (freeze-pump-thaw)	65
3	CH ₂ Br ₂ instead of CH ₂ Cl ₂	20
4	THF instead of CH ₂ Cl ₂	63
5	THF instead of CH_2CI_2 (freeze-pump-thaw)	52
6	DCE, hexanes, toluene instead of CH_2CI_2	24-30
7	CH_2CI_2 /cyclohexane (1:1) instead of CH_2CI_2	98
8	$CsPbBr_3$ powder instead of perovskite nanopaticle	<8
9	CsBr + PbBr ₂ instead of CsPbBr ₃	<5
10	no CsPbBr ₃ or no light	<5
A Chandard	reaction conditions: this hand (fe 0.2 mms). Co	DhDr (1 mol ⁰ () on

^a Standard reaction conditions: thiophenol (**1a**, 0.2 mmol), CsPbBr₃ (1 mol%), and CH₂Cl₂ (4 mL) at room temperature for 6 h. ^b NMR yields with 1,3,5-trimethoxybenzene as the internal standard.

S11a, see ESI^T). However, the transformation was even more efficient without special deoxygenation treatment (entry 1 vs. 2), enabling a convenient operation protocol. CH_2Cl_2 was the most effective solvent among those tested (entries 3, 4 and 6). A mixed solvent system CH_2Cl_2 /cyclohexane (1:1, v/v) afforded an equally good yield to that with CH_2Cl_2 alone (entry 7). Bulk perovskites (entries 8-9) were shown to exhibit much lower catalytic activity, indicating that the reactions occurred on the large surface areas offered by the nanocrystals. Crucially, the absence of either the catalyst or light (entry 10) gave negligible reaction yields, confirming the photocatalytic nature of the reaction. The computed external quantum yield of this thiol coupling was 3.6%, which is reasonably high compared to other semiconductor-catalyzed non-radical chain-based photo chemical transformations (e.g., β -alkylation using CdSe QD as the catalyst).⁹

The photocatalytic activity of perovskite nanocrystals with different halide contents was subsequently tested. As shown in Table 2, the bromide-rich perovskites gave the highest reaction yields (entries 2 and 3). The smallest-bandgap iodide perovskite offered a lower yield of 58% (entry 1) due to its lower oxidative potential compared to CsPbBr₃. The reaction was significantly less active for the larger-bandgap chloride-rich perovskites (entries 5-6), and this is due to the material's low extinction coefficient in the visible range, hence causing lower photoexcitation efficiency by white LEDs (Fig. 1b). However, photoexcitation with a 400 nm UV LED allows a high reaction yield (93%) to be obtained using CsPbCl₃ catalyst (entry 7). In addition, an in-situ halide exchange using CsPbCl₃ with bromine,⁴⁸ can also trigger this reaction and turn CsPbCl₃ into an effective photocatalyst under visible-light (entries 8-9). TEM and HR-TEM images (Fig. 2) have also shown the perovskite cuboidal nanocrystalline structure and size distribution to be preserved at the end of an 8-hour reaction, hence suggesting that the catalyst was robust and reusable. The reusability of the catalyst was investigated in CH₂Cl₂/cyclohexane mixed solvent under white

Journal Name

LED irradiation for consecutive three batches of thiophenol coupling, achieving 98%, 95%, and 90% NMR yield respectively (Fig. S9a, see ESI^{\dagger}), which indicated a good reusability of the nanocrystalline perovskite catalyst.

Table 2 Reaction investigation using CsPbX₃ perovskite catalysts with different halogen contents^{*a*}

2 X	SH	CsPbX ₃ perovskite (1 mol%) CH ₂ Cl ₂ , white LEDs, rt, air, 6 h	- S'S
_	1a		2a
	Entry	CsPbX ₃ perovskite	Yield of 2a (%) ^b
	1	CsPbl ₃	58
	2	CsPbBr ₃	98
	3	CsPbBr ₂ Cl	98
	4	CsPbBr _{1.5} Cl _{1.5}	68
	5	CsPbBrCl ₂	35
	6	CsPbCl ₃	12
	7 ^c	CsPbCl ₃	93
	8	CsPbCl ₃ + Br ₂	62
	9	Br ₂	8

^a Reaction conditions: thiophenol (**1a**, 0.2 mmol), CsPbX₃ (1 mol%), and CH₂Cl₂ (4 mL) at room temperature for 6 h. ^b NMR yields with 1,3,5-trimethoxybenzene as the internal standard. ^c Irradiated using UV LED strip (maximum emission at 400 nm).



Fig. 2 TEM images of CsPbBr₃ NCs before and after reaction. (a) CsPbBr₃ NCs, (b) 1 mol% CsPbBr₃ NCs with PhSH in CH_2CI_2 under white LEDs irradiation for 8 h, (c) HR-TEM image of CsPbBr₃ NCs, (d) HR-TEM image of 1 mol% CsPbBr₃ NCs with PhSH in CH_2CI_2 under white LEDs irradiation for 8 h.

The optimized photocatalytic protocol was then applied to convert a broad range of thiols into their corresponding disulfides (Table 3). The couplings were quite efficient with aromatic substrates, no matter with electron-rich, electron-poor, or heterocyclic aryl substituents (**2a-2e**). Aliphatic thiols can be converted into the disulfides in excellent yields as well (**2f-2h**),

except the sterically demanding substrate tert-butyl mercaptan **1i** which showed a less efficient transformation (82% conversion).

Table 3 Substrate scope of symmetric and unsymmetrical disulfides formation $^{\sigma}$



^a Standard reaction conditions: thiols (**1a-i**, 0.2 mmol), CsPbBr₃ (1 mol%), and CH₂Cl₂ (4 mL) at room temperature under white LED for 12 h. Average isolated yields of two runs.
^b Ar-SH (**1a**, **1e** and **1i**, 0.2 mmol), AlkyI-SH (**2h** and **2i**, 0.3 mmol). ^c Ratios and conversions based the crude ¹H NMR spectra.

We further tested the formation of unsymmetrical disulfides, as they are important bioactive compounds, with some showing promise in clinical evaluation for tumor treatment.⁴⁹⁻⁵⁰ As illustrated in Table 3, by mixing one equivalent of an aryl thiol and 1.5 equivalent of an aliphatic thiol in the presence of the perovskite nanocrystal catalyst under visible-light-irradiation, unsymmetrical aryl alkyl disulfides 2j to 2l were produced in high selectivity (more than statistical 3:1 ratio of hetero- to homo-disulfides). A time-scale study (Fig. S1, see ESI⁺) indicated that the better selectivity may originate from the fact that the aryl thiyl radicals generated are more reactive than alkyl thiyl radicals, and the aryl-aryl disulfide intermediate can react with alkyl thivl radicals to generate the desired unsymmetrical alkyl aryl sulfide, while the slowly generated dialkyl sulfide cannot.⁵¹ This photocatalytic protocol provides a mild way to selectively prepare certain types of unsymmetrical disulfides in an atom- and step-economic way.

In order to elucidate the reaction mechanisms, we measured the PL intensity of $CsPbBr_3$ and $CsPbI_3$ perovskites with different added concentrations of thiophenol, as shown in Fig. 3a and 3b. An unexpected enhancement in the PL of $CsPbBr_3$ and $CsPbI_3$ was observed upon the addition of thiophenol. Such behavior deviates markedly from typical photocatalytic reactions where both electron-transfer and energy-transfer processes from the photocatalyst to the substrates lead to PL quenching. The PL enhancement observations here could be rationalized by the

ARTICLE

Published on 24 July 2018. Downloaded by University of Sussex on 7/25/2018 12:05:06 PM

coordination of the thiol group to the nanocrystal surface at Pb-rich defective sites, thereby passivating the surface and shutting off non-radiative Shockley-Read-Hall recombination. The binding of thiols to the Pb atoms on the surface of perovskites has also been confirmed by a characteristic Pb–S bond peak around 800 cm⁻¹ in the FTIR spectra (Fig. S13, see ESI[†]).⁵² Our observations suggest that the efficacy of a photocatalytic reaction may not necessarily be inferred via PL quenching, as typically described by the Stern-Volmer relationship, since adventitious factors such as defect passivation could completely mask and overpower any charge transfer quenching effects.

Based on the accumulated experimental evidence, we propose plausible mechanisms for the thiol coupling in Fig. S15 (See ESI[†]). First, the thiol S and H coordinates to Pb and Br respectively. Upon photo-excitation, the electron in the perovskite conduction band transfers to the proton while the hole in the valence band transfers to the mercaptan group, leading to the formation of a hydrogen radical and a thiyl radical (see ESI[†] for the experimental support towards generation of thiyl radicals). The former will couple to produce H_2 while the thiyl radicals couple to form the corresponding disulfides on the surface of the catalyst. In the presence of air, O_2 can be reduced by accepting electrons in the conduction band of CsPbBr₃ to give superoxide (O_2^{-1}) (E^{red} [O_2/O_2^{-1}] = -0.8 V vs. SCE], which may promote the thiol coupling.

During our experiments, we discovered that the absorbance edge of the perovskite nanocrystals blue-shifted monotonically from 530 nm to 440 nm over the course of the reaction, as shown in Fig. S12 (See ESI^T). Such spectral shifts are reminiscent of bandgap changes due to halide exchange reactions, which is well-reported for lead halide perovskites mixed with other ionic halide sources.^{37,} ⁵³⁻⁵⁴ In our case, this spectral shift is a result of a slow photoactivated halide exchange of the bromide perovskites with the CH₂Cl₂ solvent, which indicated a perovskite-promoted C-Cl bond cleavage. The photo-promoted anion exchange between CsPbBr₃ with CH₂Cl₂ has been confirmed by XRD study of the perovskite nanocrystals before and after reaction, as well as the detection of bromochloromethane of the reaction product mixture. We conducted the experiments in the dark and confirmed that there were no spectral shifts in the perovskite, indicating that this halide exchange reaction with dichloromethane was photo-activated. Spectral shifts were also observed when experiments were conducted in the absence of thiophenol, hence showing that the halide exchange was independent of the thiol-coupling process. Detailed study on the mechanism, scope evaluation, and its application to access full-spectral tuning of perovskite photoluminescence from red to violet will be reported in another report.

2.2 Perovskite catalyzed dehydrogenative C–P coupling reactions of tertiary amines with phosphite esters

The direct use of C–H bonds for cross-coupling reactions is a primary goal for green organic synthesis due to its atom- and stepeconomy. The cross-dehydrogenative coupling (CDC) reaction of the C–H bond adjacent to an amino nitrogen atom represents an important synthetic strategy as the nitrogen-containing pharmaceutical compounds presented a substantial level of structural complexity.⁵⁵ To further demonstrate the utility of perovskite photocatalysts for organic synthesis, we show that the cesium lead perovskite nanocrystals can be effectively applied for C–H activation by evaluating the phosphonylation of *N*-aryl tetrahydroisoquinoline derivatives and simple tertiary amines (for optimization, see ESI[†], Table S1).⁵⁶⁻⁵⁸ As shown in Table 4, by the employment of 1 mol% of CsPbBr₃ in toluene under white LED irradiation, a range of phosphite esters **4** can undergo the CDC with *N*-phenyl tetrahydrosioquinoline to deliver phosphonylation products **5a-5d** in good to excellent yields. Both electron-rich and electron-deficient substituents on the *N*-aryl or the isoquinoline ring retained the high reactivity (**5e-5k**). Notably, the perovskite photocatalysis strategy could be applied to more challenging simple acyclic and cyclic tertiary amines to produce



Fig. 3 PL intensity of (a) $CsPbBr_3$ in THF and (b) $CsPbI_3$ in CH_2Cl_2 with different added concentrations of thiophenol.

the corresponding C–P coupling product (**5I** and **5m**) in moderate efficiency. On the other hand, *N*-methylmorpholine cannot give the desired product (**5n**). Similar to thiol coupling, the phosphonylation proceeded under strict air-free environment with evolution of molecular hydrogen gas (Fig. S11b, see ESI^{\dagger}), however, it became more efficient without any special degassing treatment. Finally, we examined the recyclability and reusability of the CsPbBr₃ perovskite for this phosphonylation. It was found that the catalyst could be reused at least five times without a noticeable loss of catalytic activity (Fig. S10, see ESI^{\dagger}).

Journal Name

The luminescence quenching study showed that both the tetrahydroisoquinoline and phosphite would enhance the PL of CsPbBr₃ at low concentration (Fig. S14, see ESI[†]), indicating the coordination of both substrates to the perovskite nanocrystal surface. However, PL quenching of CsPbBr₃ was observed when further increasing the amount of tetrahydroisoquinoline or phosphite, with a higher quenching rate associated with tetrahydrosioquinoline, which may suggest an electron-transfer between the photocatalyst and the substrates. A plausible mechanism was thus proposed for the perovskite-catalyzed phosphonylation (Fig. S16, see ESI[†]). Upon irradiation by visible-light, the electron in the perovskite conduction band transfers to molecular O₂ to form superoxide radical anion O₂⁻⁻, while the hole in the valence band transfers to the amine substrate on the catalyst

Table 4Substrate scope of cross-dehydrogenative couplingbetween tertiary amines and phosphite esters



^a Standard reaction conditions: **3** (0.1 mmol), **4** (0.12 mmol, 1.1 equiv), CsPbBr₃ (1 mol%), and toluene (1.5 mL) at room temperature under white LED for 4 h. ^b Average isolated yields of two runs. ^c THF as solvent. ^d CsPbBr₃ (5 mol%), THF as solvent. ^e No reaction.

surface to generate a radical cation intermediate. The active species O_2^{-} subsequently abstracts a proton from the radical cation intermediate to form an α -amino radical, which will be further oxidized to an imine cation. The deprotonated phosphite nucleophiles will attack the imine cation to yield the final coupling product.

3. Conclusions

Our study has demonstrated the potential of using perovskite semiconductors as photocatalysts in organic synthesis. Their

remarkable potential lies in the materials' large extinction coefficients, broad absorption spectra, facile bandgap tuning, rich surface chemistry, and easy fabrication. We have demonstrated a clean, mild, and efficient oxidative coupling of thiols to symmetric disulfides with or without external oxidants, and further extended the protocol to prepare valuable unsymmetrical disulfides. The subsequent discovery of a visible-light-mediated crossdehydrogenative coupling between tertiary amines and phosphite esters further illustrates that the perovskite nanocrystals can activate a variety of organic substrate patterns, and offer an initial blueprint towards its utilization in a diverse range of photocatalyzed organic transformations. The easy fabrication of perovskite nanocrystals also indicates their potential applications in continuous-flow synthesis, and these studies are ongoing in our laboratories.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

The authors are grateful for the financial support provided by the National University of Singapore (R-143-000-665-114, R-143-000-696-114, and R-143-000-674-114) and A*STAR RIE2020 AME (R-143-000-690-305).

Notes and references

§ Abbreviations: SCE, Saturated calomel electrode; PL, Photoluminescence.

- 1 N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075-10166.
- 2 D. Ravelli, S. Protti and M. Fagnoni, Chem. Rev., 2016, 116, 9850-9913.
- 3 K. L. Skubi, T. R. Blum and T. P. Yoon, *Chem. Rev.*, 2016, **116**, 10035-10074.
- 4 C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322-5363.
- 5 J. Xuan and W.-J. Xiao, Angew. Chem. Int. Ed., 2012, **51**, 6828-6838.
- 6 J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102-113.
- 7 X.-B. Li, Z.-J. Li, Y.-J. Gao, Q.-Y. Meng, S. Yu, R. G. Weiss, C.-H. Tung and L.-Z. Wu, Angew. Chem. Int. Ed., 2014, 53, 2085-2089.
- 8 Z. Chai, T.-T. Zeng, Q. Li, L.-Q. Lu, W.-J. Xiao and D. Xu, J. Am. Chem. Soc., 2016, **138**, 10128-10131.
- 9 J. A. Caputo, L. C. Frenette, N. Zhao, K. L. Sowers, T. D. Krauss and D. J. Weix, *J. Am. Chem. Soc.*, 2017, **139**, 4250-4253.
- 10 M. Cherevatskaya, M. Neumann, S. Füldner, C. Harlander, S. Kümmel, S. Dankesreiter, A. Pfitzner, K. Zeitler and B. König, Angew. Chem. Int. Ed., 2012, 51, 4062-4066.
- 11 Z. Zhang, K. Edme, S. Lian and E. A. Weiss, J. Am. Chem. Soc., 2017, **139**, 4246-4249.
- 12 L.-M. Zhao, Q.-Y. Meng, X.-B. Fan, C. Ye, X.-B. Li, B. Chen, V. Ramamurthy, C.-H. Tung and L.-Z. Wu, *Angew. Chem. Int. Ed.*, 2017, **56**, 3020-3024.
- 13 S. C. Jensen, S. B. Homan and E. A. Weiss, J. Am. Chem. Soc., 2016, 138, 1591-1600.

This journal is © The Royal Society of Chemistry 20xx

Published on 24 July 2018. Downloaded by University of Sussex on 7/25/2018 12:05:06 PM

- 14 C. M. Bernt, P. T. Burks, A. W. DeMartino, A. E. Pierri, E. S. Levy, D. F. Zigler and P. C. Ford, *J. Am. Chem. Soc.*, 2014, **136**, 2192-2195.
- 15 B. I. Ipe and C. M. Niemeyer, Angew. Chem. Int. Ed., 2006, 45, 504-507.
- 16 D. C. Fabry, Y. A. Ho, R. Zapf, W. Tremel, M. Panthofer, M. Rueping and T. H. Rehm, *Green Chem.*, 2017, **19**, 1911-1918.
- 17 S. P. Pitre, T. P. Yoon and J. C. Scaiano, *Chem. Commun.*, 2017, **53**, 4335-4338.
- 18 C. D. McTiernan, X. Leblanc and J. C. Scaiano, ACS Catal., 2017, 7, 2171-2175.
- 19 C. Bottecchia, N. Erdmann, P. M. A. Tijssen, L.-G. Milroy, L. Brunsveld, V. Hessel and T. Noël, *ChemSusChem*, 2016, 9, 1781-1785.
- 20 C. Vila and M. Rueping, Green Chem., 2013, 15, 2056-2059.
- 21 L. Cermenati, A. Albini, L. Cermenati, C. Richter and A. Albini, *Chem. Commun.*, 1998, 805-806.
- 22 G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar and T. C. Sum, *Science*, 2013, **342**, 344-347.
- 23 S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, **342**, 341-344.
- 24 Y. Chen, M. He, J. Peng, Y. Sun and Z. Liang, *Adv. Sci.*, 2016, **3**, 1500392.
- 25 A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, J. Am. Chem. Soc., 2009, 131, 6050-6051.
- 26 M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643-647.
- J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Gratzel, *Nature*, 2013, **499**, 316-319.
- 28 H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Grätzel and N.-G. Park, *Sci. Rep.*, 2012, 2, 591.
- 29 N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu and S. I. Seok, Nat. Mater., 2014, 13, 897-903.
- 30 W. Wang, M. O. Tade and Z. Shao, Chem. Soc. Rev., 2015, 44, 5371-5408.
- 31 Z. K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos, D. Credgington, F. Hanusch, T. Bein, H. J. Snaith and R. H. Friend, Nat. Nanotechnol., 2014, 9, 687-692.
- 32 H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend and T.-W. Lee, *Science*, 2015, **350**, 1222-1225.
- 33 N. Wang, L. Cheng, R. Ge, S. Zhang, Y. Miao, W. Zou, C. Yi, Y. Sun, Y. Cao, R. Yang, Y. Wei, Q. Guo, Y. Ke, M. Yu, Y. Jin, Y. Liu, Q. Ding, D. Di, L. Yang, G. Xing, H. Tian, C. Jin, F. Gao, R. H. Friend, J. Wang and W. Huang, *Nat. Photon.*, 2016, **10**, 699-704.
- 34 M. Yuan, L. N. Quan, R. Comin, G. Walters, R. Sabatini, O. Voznyy, S. Hoogland, Y. Zhao, E. M. Beauregard, P. Kanjanaboos, Z. Lu, D. H. Kim and E. H. Sargent, *Nat. Nano*, 2016, **11**, 872-877.
- 35 Q. A. Akkerman, V. D'Innocenzo, S. Accornero, A. Scarpellini, A. Petrozza, M. Prato and L. Manna, J. Am. Chem. Soc., 2015, 137, 10276-10281.
- 36 G. Li, F. W. R. Rivarola, N. J. L. K. Davis, S. Bai, T. C. Jellicoe, F. de la Peña, S. Hou, C. Ducati, F. Gao, R. H. Friend, N. C. Greenham and Z.-K. Tan, *Adv. Mater.*, 2016, **28**, 3528-3534.
- 37 L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692-3696.
- 38 H. Huang, H. Yuan, K. P. F. Janssen, G. Solís-Fernández, Y. Wang, C. Y. X. Tan, D. Jonckheere, E. Debroye, J. Long, J. Hendrix, J. Hofkens, J. A. Steele and M. B. J. Roeffaers, ACS Energy Lett., 2018, 3, 755–759.

- 39 P. Schulz, E. Edri, S. Kirmayer, G. Hodes, D. Cahen and A. Kahn, *Energy Environ. Sci.*, 2014, **7**, 1377-1381.
- 40 K. T. Butler, J. M. Frost and A. Walsh, *Mater. Horiz.*, 2015, **2**, 228-231.
- 41 V. T. Maulik, S. L. Jennifer and J. S. Teruna, *Curr. Protein Pept. Sci.*, 2009, **10**, 614-625.
- 42 B. Heras, M. Kurz, S. R. Shouldice and J. L. Martin, Curr. Opin. Struct. Biol., 2007, 17, 691-698.
- 43 R. J. Cremlyn, An Introduction to Organosulfur Chemistry, Wiley-VCH, New York, 1996.
- 44 D. Witt, Synthesis, 2008, 2491-2509.
- 45 H. J. Kim, J. H. Yoon and S. Yoon, J. Phys. Chem. A, 2010, 114, 12010-12015.
- 46 M. Oba, K. Tanaka, K. Nishiyama and W. Ando, J. Org. Chem., 2011, 76, 4173-4177.
- 47 A. Talla, B. Driessen, N. J. W. Straathof, L.-G. Milroy, L. Brunsveld, V. Hessel and T. Noël, Adv. Synth. Catal., 2015, 357, 2180-2186.
- 48 D. Solis-Ibarra, I. C. Smith and H. I. Karunadasa, Chem. Sci., 2015, 6, 4054-4059.
- 49 R. K. Ramanathan, J. Abbruzzese, T. Dragovich, L. Kirkpatrick, J. M. Guillen, A. F. Baker, L. A. Pestano, S. Green and D. D. Von Hoff, *Cancer Chemother. Pharmacol.*, 2011, **67**, 503-509.
- 50 R. K. Ramanathan, D. L. Kirkpatrick, C. P. Belani, D. Friedland, S. B. Green, H.-H. S. Chow, C. A. Cordova, S. P. Stratton, E. R. Sharlow, A. Baker and T. Dragovich, *Clin. Cancer Res.*, 2007, 13, 2109-2114.
- 51 J. Yuan, C. Liu and A. Lei, Org. Chem. Front., 2015, 2, 677-680.
- 52 Z. Liu, Y. Bekenstein, X. Ye, S. C. Nguyen, J. Swabeck, D. Zhang, S.-T. Lee, P. Yang, W. Ma and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2017, **139**, 5309-5312.
- 53 D. M. Jang, K. Park, D. H. Kim, J. Park, F. Shojaei, H. S. Kang, J.-P. Ahn, J. W. Lee and J. K. Song, *Nano Lett.*, 2015, **15**, 5191-5199.
- 54 G. Nedelcu, L. Protesescu, S. Yakunin, M. I. Bodnarchuk, M. J. Grotevent and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 5635-5640.
- 55 L. Shi and W. Xia, Chem. Soc. Rev., 2012, 41, 7687-7697.
- 56 X.-Z. Wang, Q.-Y. Meng, J.-J. Zhong, X.-W. Gao, T. Lei, L.-M. Zhao, Z.-J. Li, B. Chen, C.-H. Tung and L.-Z. Wu, *Chem. Commun.*, 2015, **51**, 11256-11259.
- 57 W.-J. Yoo and S. Kobayashi, *Green Chem.*, 2014, **16**, 2438-2442.
- 58 M. Rueping, S. Zhu and R. M. Koenigs, Chem. Commun., 2011, 47, 8679-8681.

6 | J. Name., 2012, 00, 1-3



Cesium lead halide perovskite nanocrystals have been the first time utilized as photocatalysts for organic bond formations.