Green Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Li, Y. Li, Y. Huang, T. Zhang, Y. Liu, B. Yang, C. He, X. Zhou and J. Zhang, *Green Chem.*, 2017, DOI: 10.1039/C6GC03558B.

View Article Online
DOI: 10.1039/C6GC03558B

Journal Name

COMMUNICATION

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

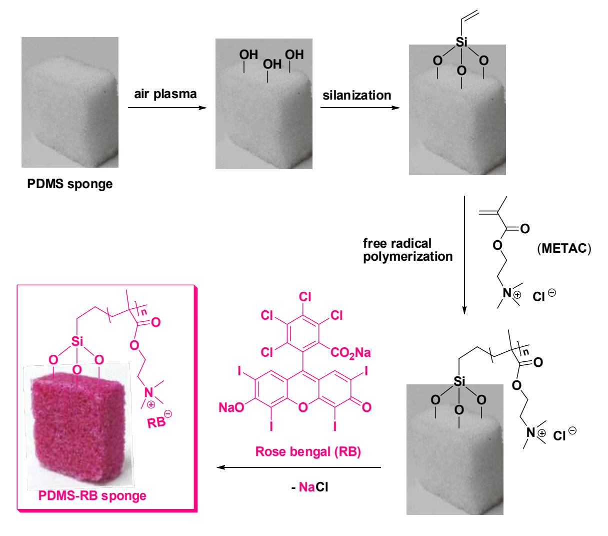
Polydimethylsiloxane organic sponge photocatalyst: high efficiency and reusability for visible light mediated cross-dehydrogenative coupling reactions†

Xingrong Li,‡ Yaoyao Li,‡ Yuxing Huang, Teng Zhang, Yizhen Liu, Bo Yang, Chuanxin He, Xuechang Zhou and Junmin Zhang*

The successfully developed polydimethylsiloxane (PDMS, a green and highly transparent polymer material) sponge photocatalyst can catalyze cross-dehydrogenative coupling (CDC) of tertiary amines and various nucleophiles with high efficiency and reusability under visible light irradiation. Through an easy-to-build continuous flow reactor, the sponge photocatalytic reaction can be facilely scaled up.

Visible-light photocatalysis,[1,2] which only needs sunlight or household lamps for irradiation, has attracted great interest in recent years based on the purpose of developing novel, green and sustainable synthetic methods under mild reaction conditions. Both transition metal and organic dye based photocatalysts have been successfully applied in various organic transformations, such as Ru, Ir complexes, as well as Rose Bengal, eosin Y, etc.[1,2] Since most of the reactions were carried out in homogeneous systems, therefore, it is difficult to recycle the catalysts for reusing. Clearly, a straightforward solution for this challenge is the immobilization of photocatalysts onto insoluble solid-state materials, resulting in a heterogeneous catalyst. In this regard, several types of materials, such as silicas,[3] polymers,[4] metal-organic frameworks (MOFs)[5] and graphene[6] have been used as support for this purpose. However conventional filtration or centrifugation is required for the recycle of these kinds of immobilized catalysts as they are generally small solid particles. The extra separation process greatly limited their reusability and practical application in industry.

In order to make immobilized photocatalyst more convenient for separation and more practical for industrial application, we envisaged that sponge as catalyst carrier would be a good candidate,[7] as the ideal catalytic process will be sucking the reactants into the sponge catalyst and squeezing out the products after the reaction, and obviously the sponge catalyst could be very easily separated for reusing from the reaction system. To achieve this purpose, the material of sponge support should be highly transparent to let the light smoothly penetrate for the photocatalysis. Polydimethylsiloxane (PDMS) is a green and highly transparent polymer material which can be used for the fabrication of contact lenses.[8]



Scheme 1 Preparation of PDMS-RB sponge photocatalyst.

Therefore we chose PDMS for making the sponge support. Using a conventional sugar-templating method, PDMS sponge can be easily prepared.[9] By anchoring organic photocatalyst on this polymer sponge, we assuming this novel heterogeneous catalyst can gain advantages in separation comparing to the reported immobilized organic photocatalysts. Instead of conventional filtration or centrifugation, we can separate the catalyst from the reaction system by simply grabbing the PDMS sponge out of the reaction mixtures. A challenge for immobilizing organic photocatalyst is the chemical inertness of PDMS material. In this study, we used the technology of surface modification (air plasma treatment) for introducing hydroxyl group on the surface of PDMS and consequently

---

College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, 518060, P. R. China. E-mail: zhangjm@szu.edu.cn

† Electronic Supplementary Information (ESI) available: Detailed experimental procedures and characterization data. See DOI: 10.1039/x0xx00000x

‡ These authors contributed equally.

DOI: 10.1039/C6GC03558B

connecting of polymer brush to successfully solve the problem.[10] Herein we reported the ionic immobilization of Rose Bengal (RB) onto post modified PDMS sponge by ionic change (Scheme 1). The obtained supported catalyst (PDMS-RB sponge) has been proven to be an excellent visible-light photocatalyst in cross-dehydrogenative coupling (CDC) reactions. The sponge photocatalyst can be easily recovered and demonstrates high efficiency in recycling experiments.

As illustrated in Scheme 1, after air plasma treatment, PDMS sponges prepared by using a conventional sugar-templating method were first functionalized with vinyltrimethoxysilane (VTMS) by a silanization process, followed by a typical free radical polymerization step with [2-(methacryloyloxy) ethyl-trimethylammonium-chloride] (METAC). The as-made PMETAC-PDMS sponges were then mixed with Rose Bengal (RB) disodium salt in EtOH/H_2O (1:1) for ionic change to afford the corresponding PDMS-RB sponge catalyst, which was analyzed by scanning electron microscopy (SEM) and quantitative energy-dispersive X-ray spectroscopy (EDS). The morphology of PDMS-RB shown by SEM implies a porous, interconnected three-dimensional framework (Fig. 1a). EDS was employed for quantitative analysis. The results shown in Fig. 1b suggests that the elements C, N, O, Si, Cl and I are homogeneously spread on the surface of PDMS-RB sponge. The amount of RB on PDMS sponge was determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard (for details, see SI).

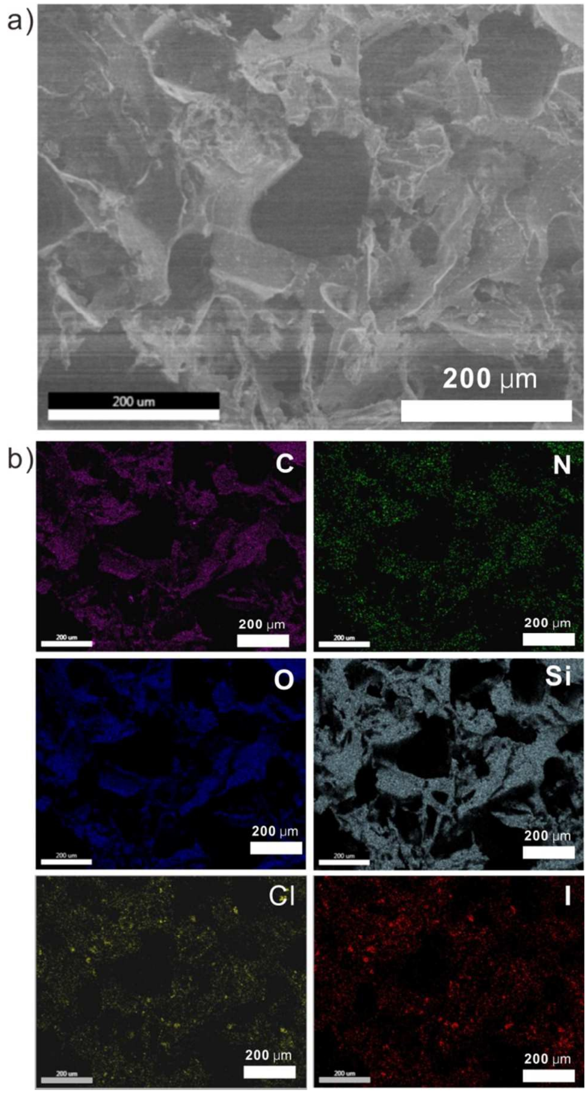
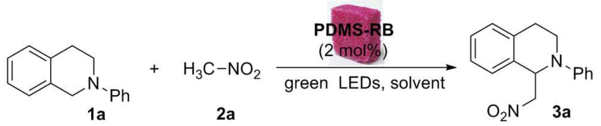


Fig. 1 (a) SEM image of PDMS-RB sponge and (b) corresponding quantitative EDS mapping of C, N, O, Si, Cl, I.

Cross-dehydrogenative coupling (CDC) reaction[11,12] is an attractive efficient and green strategy by making carbon-carbon bond directly from two different C-H bonds under oxidative conditions. To test the catalytic activity of obtained PDMS-RB sponge photocatalyst, the CDC reaction between N-phenyl tetrahydroisoquinoline and nitromethane was chose as model reaction for the investigation. As described in former reports, RB could generate the excited species RB* under visible light irradiation. RB* together with O_2 in the air can convert the tertiary amine substrate into iminium ion, which is vulnerable to the nucleophilic attack by nucleophiles.[12] Initially different solvents were screened and the results are shown in

Table 1 Optimization of reaction conditions for the PDMS-RB sponge catalyzed CDC reaction.[a]

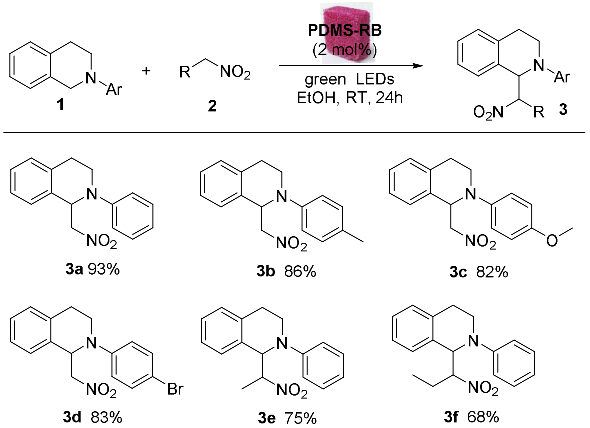


Entry	Solvent	Volume (mL)	Yield (%)[b]
1	CH_3CN	4	42
2	DMF	4	45
3	DMSO	4	39
4	DCM	4	35
5	THF	4	trace
6	Toluene	4	18
7	EtOH	4	68
8	EtOH	2	97 (93[c])/0[d]/0[e]
9	CH_3OH	2	84
10	*i*-PrOH	2	75
11	*t*-BuOH	2	39
12	H_2O	2	67/73[f]

[a] Reaction conditions: tertiary amine (0.1 mmol), nitromethane (1.0 mmol), 2 mol% PDMS-RB with different solvents, the reaction was performed in air at room temperature with 12 W green LED light belt for 24 hours. [b] Yield determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard. [c] Isolated yield. [d] Without light. [e] Without catalyst. [f] H_2O and EtOH mixture (*V*/*V*=1/1).

View Article Online
DOI: 10.1039/C6GC03558B

Table 2 PDMS-RB sponge catalyzed CDC reaction of tertiary amines and nitroalkanes.[a]

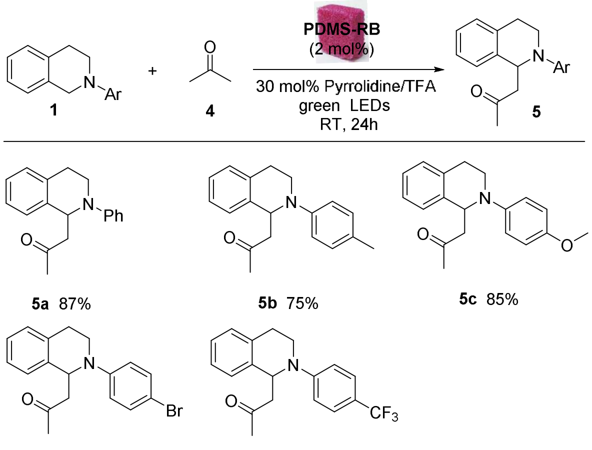


3a 93%
3b 86%
3c 82%
3d 83%
3e 75%
3f 68%

[a] Reaction conditions: tertiary amine (0.1 mmol), nitromethane (1.0 mmol), 2 mol% PDMS-RB with EtOH as solvent, the reaction was performed at room temperature with 12 W green LED light belt for 24 hours. The yields are isolated yields.

Table 1. Interestingly, when the reaction was performed in CH_3CN only moderate yield was obtained (Table 1, entry 1), however excellent yields were reported with similar conditions in homogeneous RB catalytic systems.[13] When using DMF, DMSO, and DCM as solvent, moderate yields were also obtained (Table 1, entries 2 to 4). The reaction failed when performed in THF, and afforded quite low yield in toluene (Table 1, entries 5 and 6). Finally we were delight to find out that EtOH, a greener solvent, performed best in the reaction with 68% NMR yield (Table 1, entry 7). However, the moderate yield was not satisfactory and we suspected the slow diffusion of reactants into the sponge might be the reason of the poor catalytic performance. Therefore we reduced the volume of the reaction system from 4 mL to 2 mL to increase the concentration of reactants, so that more reactants could get into the pore of the sponge to have contact with the catalytic site. Gratifyingly, we found out that the yield increased to 97% after reducing the reaction system volume (Table 1, entry 8). The performance of PDMS-RB is in CDC reaction between N-phenyl tetrahydroisoquinoline and nitromethane in ethanol is comparable with noble metal based photocatalysts, such as Ir based catalytic systems.[11] Both the visible light from the LED belt and the catalyst are essential for the reaction as no conversion was observed when the reaction was conducted either in dark environment or without the catalyst (Table 1, entry 8). Other alcohols as solvent were also tested, the results showed a trend of primary alcohol > secondary alcohol > tertiary alcohol (Table 1, entries 8-11) and EtOH was still the optimal choice of solvents. To find a more greener replacement for the solvent, H_2O and the mixture of H_2O and ethanol were tested in the reaction. The yields are good (Table 1, entry 12), but not comparable with the yield of the reaction conducted in pure ethanol. Therefore, we sticked to ethanol as the optimized solvent for further study.

Table 3 PDMS-RB sponge catalyzed dehydrogentavie-Mannich reaction of tertiary amines and acetone.[a]

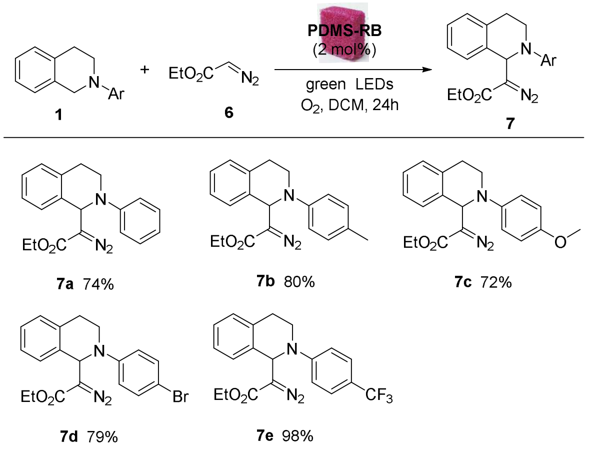


5a 87%
5b 75%
5c 85%
5d 98%
5e 97%

[a] Reaction conditions: tertiary amine (0.1 mmol), 2 mol% PDMS-RB, and 30 mol% pyrrolidine/TFA in 2 mL acetone, the reaction was performed at room temperature with 12 W green LED light belt for 24 hours. The yields are isolated yields.

With the optimized condition, we screened other substrates for this photocatalytic CDC reaction to demonstrate the broad usefulness of the sponge catalyst. As summarized in Table 2, a series of substituted tetrahydroquinoline derivatives were able to couple with nitroalkanes efficiently by affording the desired

Table 4 PDMS-RB sponge catalyzed CDC of tertiary amines and ethyl diazoacetate.[a]



7a 74%
7b 80%
7c 72%
7d 79%
7e 98%

[a] Reaction conditions: tertiary amine (0.1 mmol), ethyl diazoacetate (1.0 mmol), 2 mol% PDMS-RB sponge in 1 mL DCM, the reaction was performed at room temperature under O_2 with 12 W green LED light belt for 24 hours. The yields are isolated yields.

View Article Online
DOI: 10.1039/C6GC03558B

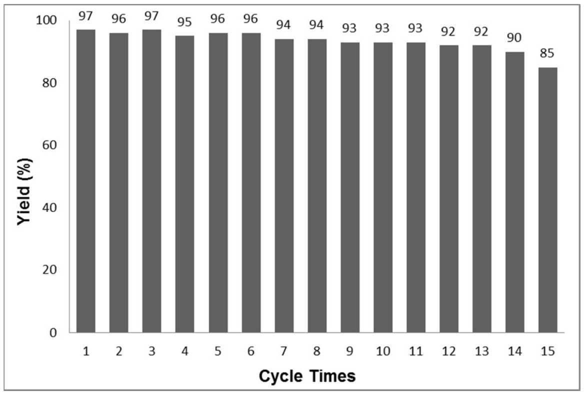


Fig. 2 Recycling experiments of PDMS-RB sponge catalyst for the CDC reaction of N-phenyl tetrahydroisoquinoline and nitromethane.

coupling products in good to excellent yields, which were comparable to literature reports.[13] The electronic effect is not prominent for the substitution groups on N-phenyl ring as the yields for electron rich and electron poor N-phenyl ring were quite close (Table 2, **3b**-**3d**). The lower yields for nitropropane and nitroethane can be attributed to the steric effect of the nucleophiles (Table 2, **3e** and **3f**).[14]

The dehydrogenative-Mannich reaction is possibly more superior than the conventional Mannich reactions for saving the extra step of preparation of the imine, as the reactive iminium intermediate is formed in situ for this method.[15] RB was reported to be an effective catalyst for this kind of reaction under visible-light irradiation.[13] To verify that the heterogeneous PDMS-RB sponge catalyst still can work effectively in this kind of reaction, several substituted tetrahydroquinoline derivatives were chose for the reaction and good to excellent yields were obtained as shown in Table 3. In this type of reaction, electron deficient tetrahydroquinoline derivatives gave the best results (Table 3, entries **5d** and **5e**).

To further explore the applications of PDMS-RB sponge catalyst in organic synthesis reactions, a series CDC reaction of tertiary amines with ethyl diazoacetate were performed.[16] The good to excellent yields were obtained as shown in Table 4. Together with the aforementioned reactions, the overall results indicate that PDMS-RB sponge has a wide range of application in organic photocatalysis.

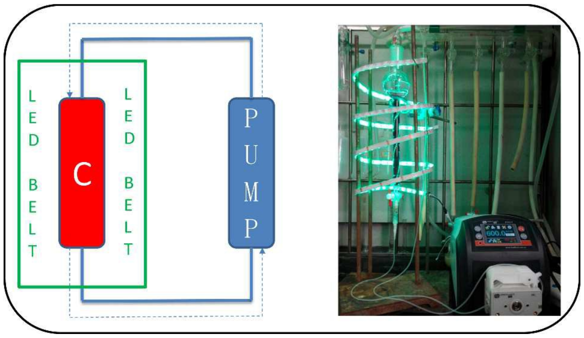


Fig. 3 Schematic illustration of the continuous flow reactor and the picture of the setup, C stands for a glass column filled with PDMS-RB sponge catalyst.

In the meantime, the recyclability of PDMS-RB sponge as a heterogeneous photocatalyst was also investigated. The model reaction of N-phenyl tetrahydroisoquinoline and nitromethane was chose for the investigation. The catalyst can be convenient removed from the reaction system by simple grabbing it out from the solution. It can be reused 15 times without significant loss of the catalytic activity, and the results are shown in Fig. 2. After 15 cycles, a small yield reduction was observed. This might due to the leaching of catalyst as it is anchored on the support by non-covalent interaction. It should be pointed out that the PDMS-RB sponge kept intact after 15 times recycling, which shows the good stability of such catalyst in ethanol. This can be attributed to the swelling property of PDMS in ethanol.[17]

To demonstrate the possible industrial application of PDMS-RB sponge catalyst, a continuous flow reactor was built up (Fig. 3). A gram scale reaction of the model reaction between N-phenyl tetrahydroisoquinoline and nitromethane was tested and 88% of isolated yield was obtained after 48 h (the catalyst loading is 1.4 mol%). This setup is quite convenient to build - one only needs a peristaltic pump, a glass column and LED belt to build such reactor (for details, see the SI). Therefore a typical organic laboratory can afford such setup and perform big scale synthesis using PDMS-RB sponge catalyst.

In conclusion, by adopting the technology of surface modification and polymer brushes synthesis of polymer material science into organic photocatalysis, we have successfully developed a facile and efficient protocol for preparing a novel organic sponge photocatalyst by anchoring rose bengal dye on PDMS sponge. This new sponge photocatalyst reveals excellent photocatalytic activity in cross-dehydrogenative coupling reactions under visible light irradiation. The sponge photocatalyst could be readily recycled and reused without significant loss of catalytic activity for fifteen cycles. The photocatalytic reaction could be facilely scaled up through an easy-to-build continuous flow reactor. These results demonstrate that PDMS sponge is a promising support for the immobilization of organic photocatalysts. The study of immobilizing other photocatalysts (including multifunctional photocatalysts) on PDMS sponge and the related more interesting transformations is currently undergoing in our lab and will be reported in due course.

Acknowledgements

We thank the generous financial supports from National Natural Science Foundation of China (21402124, 21404072 and 21605104), Training Foundation for Outstanding Young Teachers in Higher Education Institutions of Guangdong (YQ2015145), Shenzhen Science and Technology Foundation (JCYJ20150324141711702, JCYJ20150324140036849 and JCYJ20140418182819116), and the Natural Science Foundation of SZU (827000038, 201446, 201447 and 201519). We also appreciate the thoughtful suggestions from the referees.

View Article Online
DOI: 10.1039/C6GC03558B

Notes and references

1 For reviews on visible light photoredox catalysis, see: (a) J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.,* 2011, **40**, 102; (b) J. Xuan and W. J. Xiao, *Angew. Chem.,* 2012, **124**, 6934; *Angew. Chem. Int. Ed.,* 2012, **51**, 6828; (c) D. Ravelli and M. Fagnoni, *Chemcatchem,* 2012, **4**, 169; (d) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.,* 2013, **113**, 5322; (e) M. Reckenthaler and A. G. Griesbeck, *Adv. Synth. Catal.,* 2013, **355**, 2727; (f) D. P. Hari and B. Konig, *Chem. Commun.,* 2014, **50**, 6688; (g) S. Fukuzumi and K. Ohkubo, *Org. Biomol. Chem.,* 2014, **12**, 6059; (h) J. W. Beatty and C. R. J. Stephenson, *Acc. Chem. Res.,* 2015, **48**, 1474; (i) R. A. Angnes, Z. Li, C. R. D. Correia and G. B. Hammond, *Org. Biomol. Chem.,* 2015, **13**, 9152; (j) X. J. Lang, J. C. Zhao and X. D. Chen, *Chem. Soc. Rev.,* 2016, **45**, 3026; (k) M. H. Shaw, J. Twilton and D. W. C. MacMillan, *J. Org. Chem.*, 2016, **81**, 6898.

2 For the journal '*Accounts of Chemical Research*' special issue "Photoredox Catalysis in Organic Chemistry", see: (a) E. C. Gentry and R. R. Knowles, *Acc. Chem. Res.,* 2016, **49**, 1546; (b) I. Ghosh, L. Marzo, A. Das, R. Shaikh and B. König, *Acc. Chem. Res.,* 2016, **49**, 1566; (c) A. C. Hernandez-Perez and S. K. Collins, *Acc. Chem. Res.,* 2016, **49**, 1557; (d) C. R. Jamison and L. E. Overman, *Acc. Chem. Res.,* 2016, **49**, 1578; (e) S. P. Pitre, C. D. McTiernan and J. C. Scaiano, *Acc. Chem. Res.,* 2016, **49**, 1320; (f) J. C. Tellis, C. B. Kelly, D. N. Primer, M. Jouffroy, N. R. Patel and G. A. Molander, *Acc. Chem. Res.,* 2016, **49**, 1429; (g) T. P. Yoon, *Acc. Chem. Res.,* 2016, **49**, 2307; (h) D. Staveness, I. Bosque and C. R. J. Stephenson, *Acc. Chem. Res.,* 2016, **49**, 2295; (i) O. Reiser, *Acc. Chem. Res.,* 2016, **49**, 1990; (j) K. Nakajima, Y. Miyake and Y. Nishibayashi, *Acc. Chem. Res.,* 2016, **49**, 1946; (k) S. A. Morris, J. Wang and N. Zheng, *A Acc. Chem. Res.,* 2016, **49**, 1957; (l) K. A. Margrey and D. A. Nicewicz, *Acc. Chem. Res.,* 2016, **49**, 1997; (m) M. Majek and A. Jacobi von Wangelin, *Acc. Chem. Res.,* 2016, **49**, 2316; (n) T. Koike and M. Akita, *Acc. Chem. Res.,* 2016, **49**, 1937; (o) M. N. Hopkinson, A. Tlahuext-Aca and F. Glorius, *Acc. Chem. Res.,* 2016, **49**, 2261; (p) J.-P. Goddard, C. Ollivier and L. Fensterbank, *Acc. Chem. Res.,* 2016, **49**, 1924; (q) D. C. Fabry and M. Rueping, *Acc. Chem. Res.,* 2016, **49**, 1969; (r) F. Dumur, D. Gigmes, J.-P. Fouassier and J. Lalevée, *Acc. Chem. Res.,* 2016, **49**, 1980; (s) J.-R. Chen, X.-Q. Hu, L.-Q. Lu and W.-J. Xiao, *Acc. Chem. Res.,* 2016, **49**, 1911; (t) T. Chatterjee, N. Iqbal, Y. You and E. J. Cho, *Acc. Chem. Res.,* 2016, **49**, 2284; (u) A. Arora and J. D. Weaver, *Acc. Chem. Res.,* 2016, **49**, 2273.

3 (a) S. Guo, H. Zhang, L. Huang, Z. Guo, G. Xiong and J. Zhao, *Chem. Commun.,* 2013, **49**, 8689; (b) A. Jana, J. Mondal, P. Borah, S. Mondal, A. Bhaumik and Y. L. Zhao, *Chem. Commun.,* 2015, **51**, 10746; (c) O. Planas, N. Macia, M. Agut, S. Nonell and B. Heyne, *J. Am. Chem. Soc.,* 2016, **138**, 2762.

4 (a) Z. G. Xie, C. Wang, K. E. deKrafft and W. B. Lin, *J. Am. Chem. Soc.,* 2011, **133**, 2056. (b) J.-X. Jiang, Y. Li, X. Wu, J. Xiao, D. J. Adams and A. I. Cooper, *Macromolecules,* 2013, **46**, 8779; (c) X. Gu, X. Li, Y. Chai, Q. Yang, P. Li adn Y. Yao, *Green Chem.,* 2013, **15**, 357; (d) Q. Sun, Z. F. Dai, X. J. Meng and F. S. Xiao, *Chem. Soc. Rev.,* 2015, **44**, 6018.

5 (a) C. Wang, Z. G. Xie, K. E. deKrafft and W. L. Lin, *J. Am. Chem. Soc.,* 2011, **133**, 13445; (b) T. Zhang and W. Lin, *Chem. Soc. Rev.,* 2014, **43**, 5982; (c) S. B. Wang and X. C. Wang, *Small,* 2015, **11**, 3097; (d) X. Yu and S. M. Cohen, *Chem. Commun.,* 2015, **51**, 9880; (e) Y. Quan, Q. Y. Li, Q. Zhang, W. Q. Zhang, H. Lu, J. H. Yu, J. Chen, X. S. Zhao and X. J. Wang, *RSC Adv.,* 2016, **6**, 23995.

6 Z. Li, W. Zhang, Q. Zhao, H. Gu, Y. Li, G. Zhang, F. Zhang and X. Fan, *ACS Sustainable Chem. Eng.*,2015, **3**, 468.

7 Sponge is a material commonly used in daily life, but its exploration in catalysis has been rare. This concept of 'Organic Sponge Catalysis' is inspired by the very impressive work 'Organotextile Catalysis' from the List group, see: J. W. Lee, T. Mayer-Gall, K. Opwis, C. E. Song, J. S. Gutmann and B. List, *Science,* 2013, **341**, 1225.

8 A. J. T. Teo, A. Mishra, I. Park, Y.-J. Kim, W.-T. Park and Y.-J. Yoon, *ACS Biomater. Sci. Eng.,* 2016, **2**, 454.

9 S.-J. Choi, T.-H. Kwon, H. Im, D.-I. Moon, D. J. Baek, M.-L. Seol, J. P. Duarte and Y.-K. Choi, *ACS Appl. Mater. Interfaces,* 2011, **3**, 4552.

10 S. Liang, Y. Li, J. Yang, J. Zhang, C. He, Y. Liu and X. Zhou, *Adv. Mater. Technol.,* 2016, **1**, 1600117.

11 For examples and reviews on cross-dehydrogenative coupling, see: (a) A. G. Condie, J. C. González-Gómez and C. R. J. Stephenson. *J. Am. Chem. Soc.,* 2010, **132**, 1464; (b) H. Bartling, A. Eisenhofer, B. König and R. M. Gschwind. *J. Am. Chem. Soc.,* 2016, **138**, 11860; (c) C.-J. Li, *Acc. Chem. Res.,* 2009, **42**, 335; (d) C. J. Scheuermann, *Chem. Asian J.,* 2010, **5**, 436; (e) W. J. Yoo and C. J. Li, in *C-H Activation,* Vol. **292** (Eds.: J. Q. Yu, Z. Shi), Springer-Verlag Berlin, Berlin, 2010, pp. 281; (f) C. S. Yeung and V. M. Dong, *Chem. Rev.,* 2011, **111**, 1215; (g) S. A. Girard, T. Knauber and C. J. Li, *Angew. Chem.,* 2014, **126**, 76; *Angew. Chem. Int. Ed.,* 2014, **53**, 74; (h) R. Ueno and E. Shirakawa, *Org. Biomol. Chem.,* 2014, **12**, 7469; (i) J. Xie, H. Jin, P. Xu and C. Zhu. *Tetrahedron Lett.,* 2014, **55**, 36; (j) J. M. Miao and H. B. Ge, *Eur. J. Org. Chem.,* 2015, 7859.

12 For examples of photocatalytic cross-dehydrogenative coupling by heterogeneous and recyclable photocatalyst, see: (a) M. Rueping, J. Zoller, D. C. Fabry, K. Poscharny, R. M. Koenigs, T. E. Weirich and J. Mayer, *Chem.-Eur. J.,* 2012, **18**, 3478; (b) L. Mohlmann, M. Baar, J. Riess, M. Antonietti, X. C. Wang and S. Blechert, *Adv. Synth. Catal.*, 2012, **354**, 1909; (c) T. Mitkina, C. Stanglmair, W. Setzer, M. Gruber, H. Kisch and B. Konig, *Org. Biomol. Chem.*, 2012, **10**, 3556; also see: refs 3-6 in this paper.

13 (a) Y. Pan, C. W. Kee, L. Chen and C.-H. Tan, *Green Chem.,* 2011, **13**, 2682; (b) for a example by similar organic dye photocatalyst eosin Y, see: D. P. Hari and B. Konig, *Org. Lett.,* 2011, **13**, 3852.

14 Q. Liu, Y.-N. Li, H.-H. Zhang, B. Chen, C.-H. Tung and L.-Z. Wu, *Chem. Eur. J.,* 2012, **18**, 620.

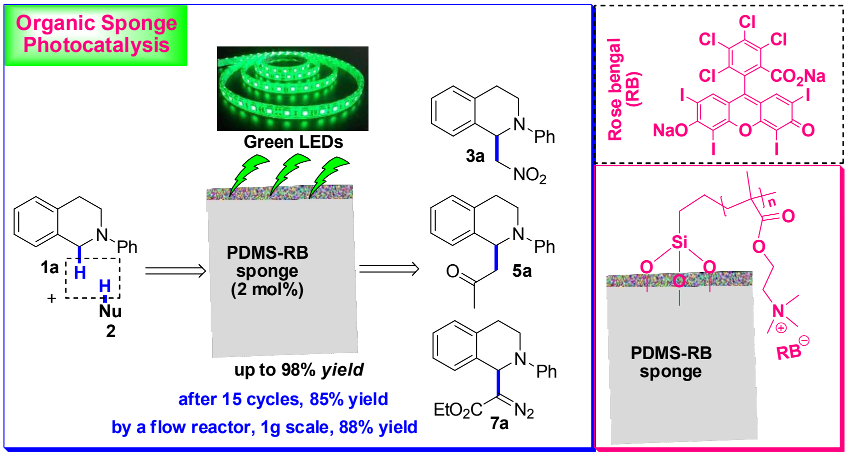
15 For examples of dehydrogenative-Mannich reaction, see: (a) A. Sud, D. Sureshkumar and M. Klussmann, *Chem. Commun.,* 2009, 3169; (b) Á. Pintér, A. Sud, D. Sureshkumar and M. Klussmann, *Angew. Chem.,* 2010, **122**, 5124; *Angew. Chem. Int. Ed.,* 2010, **49**, 5004; (c) Y. M. Shen, M. Li, S. Z. Wang, T. G. Zhan, Z. Tan and C. C. Guo, *Chem. Commun.,* 2009, 953; (d) M. Rueping, C. Vila, R. M. Koenigs, K. Poscharny and D. C. Fabry, *Chem. Commun.,* 2011, **47**, 2360; (e) J. Xie, H. Li, J. Zhou, Y. Cheng and C. Zhu, *Angew. Chem.,* 2012, **124**, 1278; *Angew. Chem. Int. Ed.,* 2012, **51**, 1252; (f) J. Zhang, B. Tiwari, C. Xing, X. Chen and Y. R. Chi, *Angew. Chem.,* 2012, **124**, 3709; *Angew. Chem. Int. Ed.,* 2012, **51**, 3649.

16 T. Xiao, L. Li, G. Lin, Z.-W. Mao and L. Zhou, *Org. Lett.,* 2014, **16**, 4232.

17 J. N. Lee, C. Park and G. M. Whitesides. *Anal. Chem.*, 2003, **75**, 6544.

View Article Online
DOI: 10.1039/C6GC03558B

Table of Contents



Organic sponge photocatalysis: green and highly transparent catalyst carrier (polydimethylsiloxane), pure organic photocatalyst, visible light source, high reusability of catalyst, easy to scale up by a flow reactor and clean cross-dehydrogenative coupling reactions; the ideal catalytic process is sucking the reactants into the sponge photocatalyst and squeezing out the products after the reaction under visible light irradiation.