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Cite this: *Chem. Sci.*, 2015, 6, 1035

Merging of the photocatalysis and copper catalysis in metal–organic frameworks for oxidative C–C bond formation†

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The direct formation of new C–C bonds through photocatalytic oxidative coupling from low reactive sp³ C–H bonds using environmentally benign and cheap oxygen as oxidant is an important area in sustainable chemistry. By incorporating the photoredox catalyst [SiW₁₁O₃₉Ru(H₂O)]⁵⁻ into the pores of Cu-based metal–organic frameworks, a new approach for merging Cu-catalysis/Ru-photocatalysis within one single MOF was achieved. The direct Cu^{II}–O–W(Ru) bridges made the two metal catalyses being synergetic, enabling the application on the catalysis of the oxidative coupling C–C bond formation from acetophenones and *N*-phenyl-tetrahydroisoquinoline with excellent conversion and size-selectivity. The method takes advantage of visible light photoredox catalysis to generate iminium ion intermediate from *N*-phenyl-tetrahydroisoquinoline under mild conditions and the easy combination with Cu-catalyzed activation of nucleophiles. Control catalytic experiments using similar Cu-based sheets but with the photoredox catalytic anions embedded was also investigated for comparison.

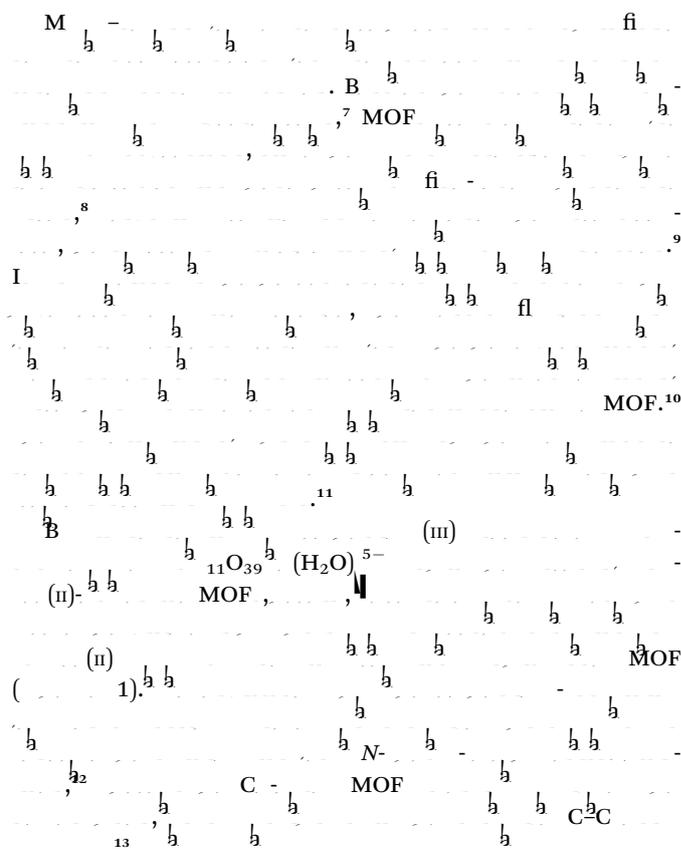
Received 5th August 2014
Accepted 27th October 2014

DOI: 10.1039/c4sc02362e

www.rsc.org/chemicalscience

Introduction

1. C–C bond formation is a key reaction in organic synthesis. 2. The direct formation of new C–C bonds through photocatalytic oxidative coupling from low reactive sp³ C–H bonds using environmentally benign and cheap oxygen as oxidant is an important area in sustainable chemistry. 3. By incorporating the photoredox catalyst [SiW₁₁O₃₉Ru(H₂O)]⁵⁻ into the pores of Cu-based metal–organic frameworks, a new approach for merging Cu-catalysis/Ru-photocatalysis within one single MOF was achieved. 4. The direct Cu^{II}–O–W(Ru) bridges made the two metal catalyses being synergetic, enabling the application on the catalysis of the oxidative coupling C–C bond formation from acetophenones and *N*-phenyl-tetrahydroisoquinoline with excellent conversion and size-selectivity. 5. The method takes advantage of visible light photoredox catalysis to generate iminium ion intermediate from *N*-phenyl-tetrahydroisoquinoline under mild conditions and the easy combination with Cu-catalyzed activation of nucleophiles. 6. Control catalytic experiments using similar Cu-based sheets but with the photoredox catalytic anions embedded was also investigated for comparison.



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† ESI[†] available free on the open access article. CCDC 997028
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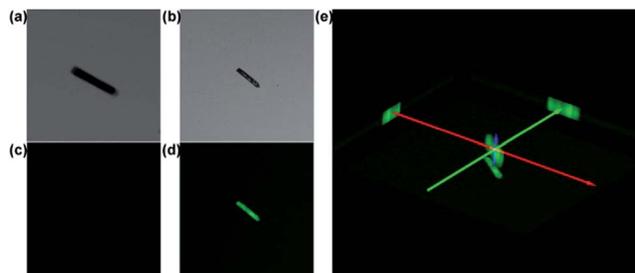


Fig. 2 Confocal images of empty (a and c) and soaked (b and d) 2',7'-dichlorofluorescein dye. Brightfield images (a and b) and confocal images (c and d) detected at $\lambda_{em} = 510\text{--}610$ nm, exited by $\lambda_{ex} = 488$ nm through a 405/488 nm filter. (e) The 3D reconstruction of the soaked 2',7'-dichlorofluorescein dye (b). Three images at the end of axes in (e) exemplify the X, Y and Z-axis projections of the soaked dye.

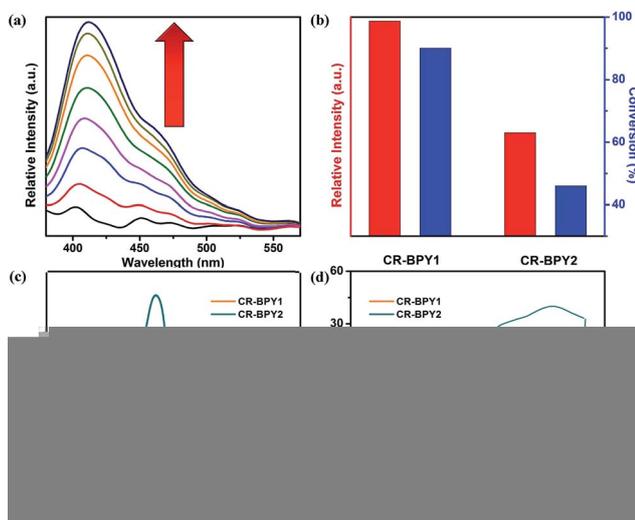
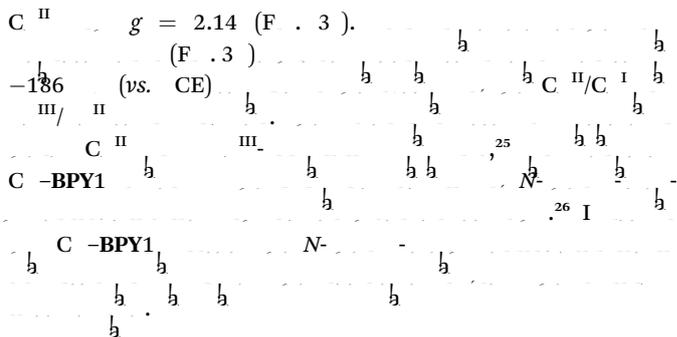


Fig. 3 (a) Family of emission spectra of CR-BPY1 (0.1% in weight) in CH_2Cl_2 suspension upon addition of *N*-phenyl-tetrahydroisoquinoline up to 0.50 mM, excitation at 362 nm. (b) The luminescence intensities of CR-BPY1 and CR-BPY2 upon addition of the same amount of *N*-phenyl-tetrahydroisoquinoline up to 0.50 mM at room temperature in CH_2Cl_2 ; the catalytic activities of CR-BPY1 and CR-BPY2 using *N*-phenyl-tetrahydroisoquinoline and nitromethane as the coupling partners. (c) EPR spectra of CR-BPY1 ($g = 2.1438$) and CR-BPY2 ($g = 2.1320$) in solid state at 77 K, respectively. (d) Solid state cyclic voltammetry of CR-BPY1 and CR-BPY2, respectively, scan rate: 50 mV s^{-1} .



Catalysis details of CR-BPY1

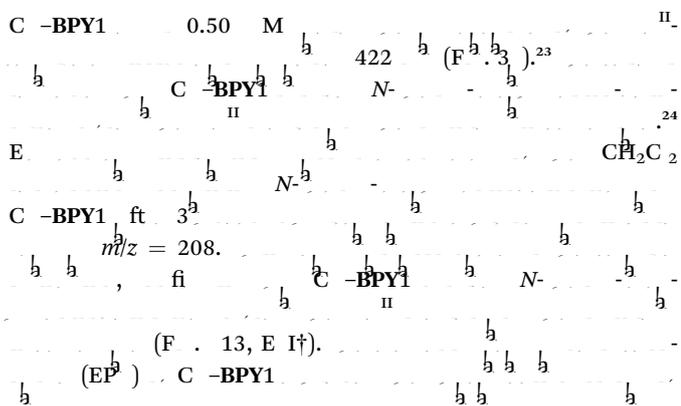
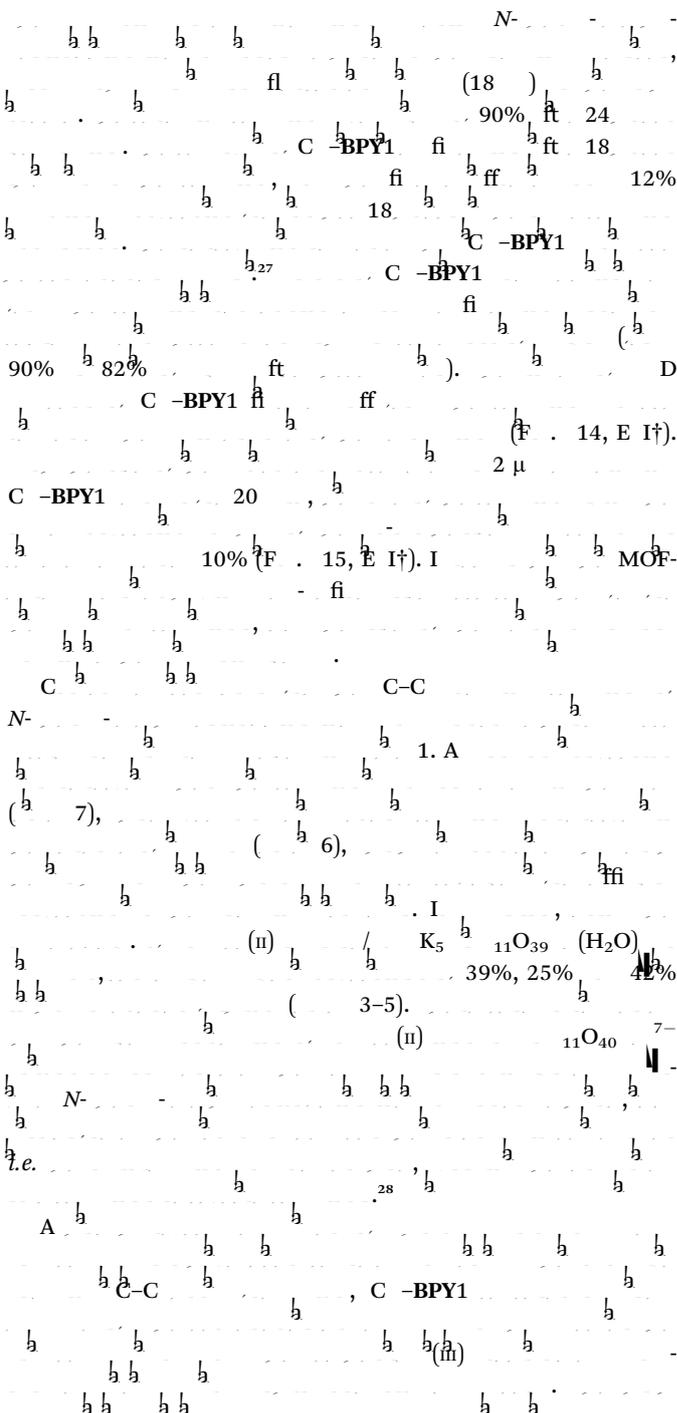


Table 1 Control experiments for the C–C coupling reaction of *N*-phenyl-tetrahydroisoquinoline and nitromethane

E	C ^a	C ^b (%)
1	C -BPY1	90
2	C -BPY2	46
3	C (NO ₃) ₂ ·3H ₂ O	39
4	K ₅ 11O ₃₉ (H ₂ O)	25
5	K ₅ 11O ₃₉ (H ₂ O) C (NO ₃) ₂ ·3H ₂ O	42
6	N	20
7	C -BPY1,	<10

^a % : *N*- (0.25), 1
^b % : 2.0 L, 18 fl, 24 ft

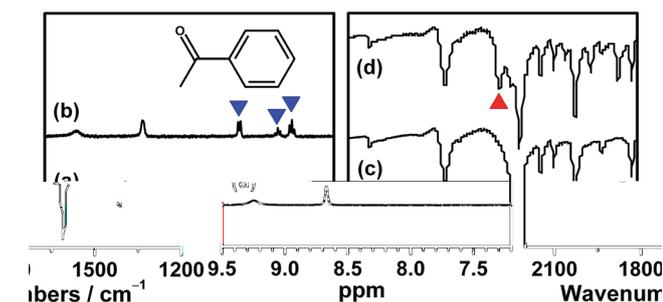
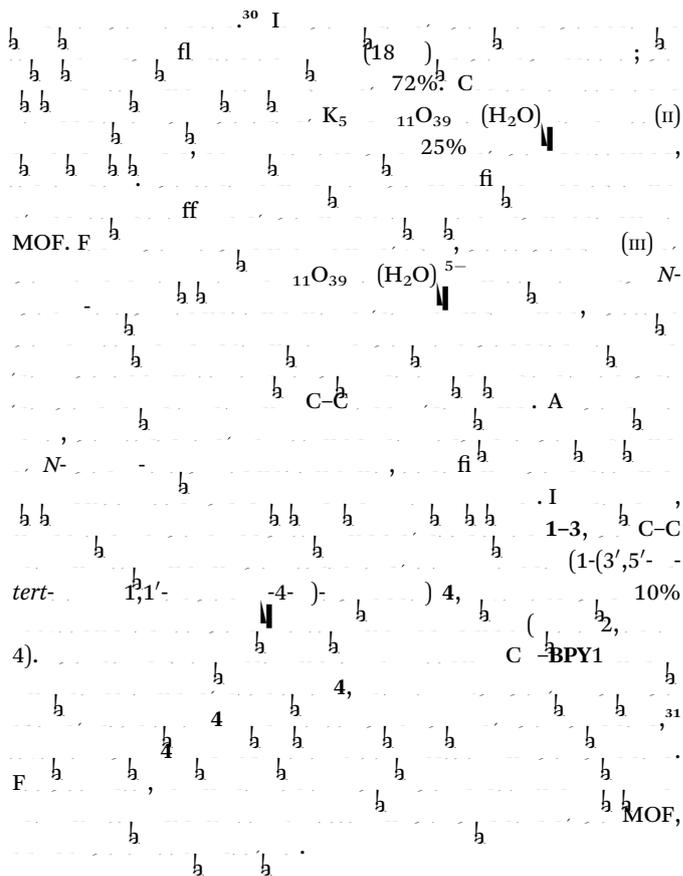
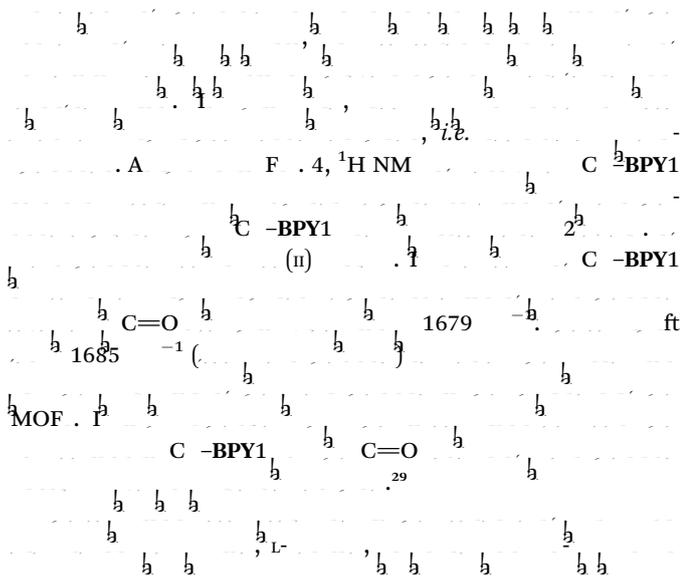
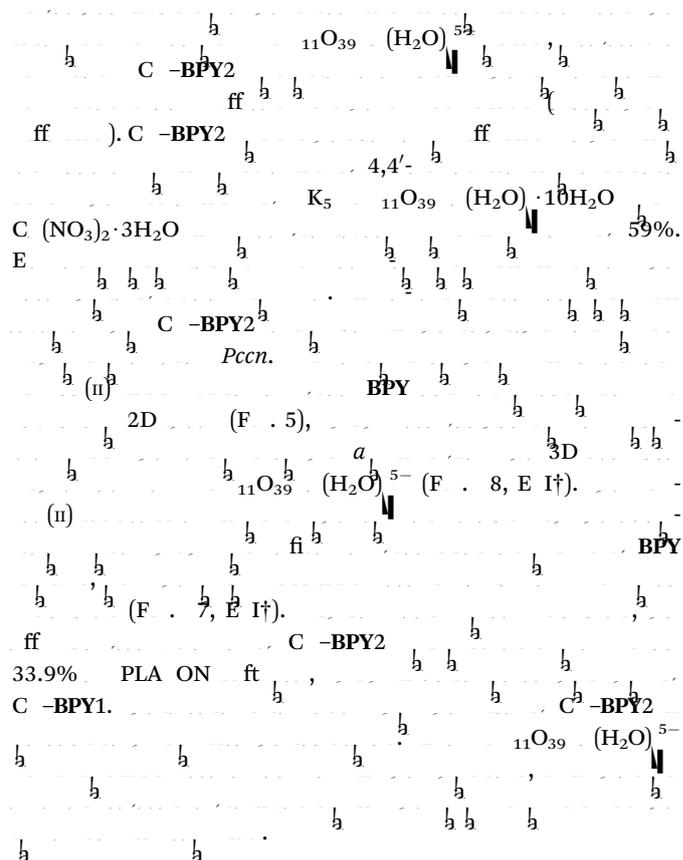


Fig. 4 ¹H NMR in DCI/DMSO and solid state IR spectra of the desolvated CR-BPY1 (a) and (c), respectively, and of the desolvated CR-BPY1 impregnated in a dichloromethane solution of acetophenone (b) and (d), respectively, showing the absorbency and activation of substrate in the MOF. The blue and red triangle represented the signals of acetophenone in the NMR and IR spectra, respectively.



Synthesis and catalytic characterizations of CR-BPY2





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