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An efficient synthesis of bifurans *via* dimerization of cyclopropenes has been successfully developed using a copper-promoted cycloisomerization and palladium-catalyzed dimerization cascade. These novel bifuran structures possess interesting optoelectronic properties.

Organic molecules bearing a heteroaryl structure motif have attracted great attention recently and are making significant contributions in different fields such as organic light emitting diodes (OLEDs),<sup>1</sup> organic field effect transistors (OFETs),<sup>2</sup> and solar cells.<sup>3</sup> Oligothiophene derivatives have been mostly highlighted in the past twenty years because of their superior electronic properties.<sup>4</sup> In 2010, Bendikov's group first reported that the oligofurans showed increased fluorescence, better packing and greater solubility than the corresponding oligothiophenes (Fig. 1).<sup>5</sup> Very recently, the same group investigated two basic units (bifuran and bithiophene) by comparing two structural isomers: TFFT and FTTF and found that the bifuran moiety is responsible for the observed better properties.5c This work demonstrates that smaller building blocks like bifurans have similar properties to longer oligofurans. In principle, incorporation of the bifuran units into organic materials should be considered a rational design of structurally-complex conjugated organic electronic materials.

Therefore, efficient synthesis of these bifuran units is of great importance. State of the art synthesis of these compounds relies on the transition-metal catalyzed cross coupling reactions (Suzuki, Negishi, Stille, *etc.*).<sup>5</sup> In these traditional coupling reactions, both heteroaryl organometallics and heteroaryl halides need to be prepared in advance. Fagnou and others reported more efficient direct arylation reactions by using aryl halides with heteroarenes.<sup>6</sup> In this approach, only one coupling partner must be preactivated (Scheme 1). Very recently, the direct oxidative C–H/C–H coupling of two heteroarenes has been reported as the most ideal synthetic



Fig. 1 Oligothiophene and oligofuran-based materials.

Dimerization of cyclopropenes to bifurans using

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tandem metal relay catalysis<sup>†</sup>

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methodology.<sup>7</sup> However, these reactions normally require very harsh conditions to achieve the twofold C–H activation. Herein, we report the synthesis of bifuran products through cycloisomerization/ dimerization of cyclopropenes *via* Tandem Metal Relay Catalysis (TMRC).<sup>8</sup> These novel multifunctionalized bifuran structures possess interesting optoelectronic properties and have potential to find applications in organic electronic materials.

Recently, we have developed an efficient copper–palladium relay catalysis (TMRC) for the synthesis of tetra-substituted alkene functionalized furans from cyclopropenes under very mild reaction conditions (Scheme 1).<sup>8</sup> Cyclopropene<sup>9</sup> underwent a copper catalyzed ring-opening/cycloisomerization reaction<sup>10</sup> and subsequent transmetallation to palladium, generating the key furan palladium intermediate **M**. This intermediate underwent an oxidative Heck reaction with alkenes generating the tetrasubstituted furans. Using this strategy, the key carbon–palladium bond was formed through a transmetallation strategy under very mild conditions. We then extended this methodology to the oxidative carbonylation of cyclo-propene for the synthesis of tetra-substituted furan carboxylate **3a**.<sup>8b</sup>



Scheme 1 Strategies for synthesis of biheteroaryl compounds.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Detailed experimental procedures and analytical data. CCDC 930435 for compound **2a**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc44762f



**Scheme 2** Copper–palladium cooperative catalyzed oxidative dimerization of cyclopropenes to bifurans.

To our great surprise, the bifuran product was obtained in 65% yield at 80  $^{\circ}$ C (Scheme 2). The structure was unambiguously characterized by NMR, mass analysis and also single X-ray crystallography.

Examining this reaction in detail, we discovered that CO was not needed. However, both copper and palladium were essential for this transformation. Under optimized reaction conditions (for details, see ESI<sup>†</sup>), Pd(OAc)<sub>2</sub> (5 mol%) and Cu(OAc)<sub>2</sub> (2 equiv.) at 80 °C, bifuran **2a** was formed in 86% yield in 3 h.

Several alkyl or aryl substituted cyclopropenes were subjected to this reaction and the results are summarized in Table 1. Alkyl substituted cyclopropene dicarboxylates reacted smoothly to generate the corresponding bifurans in 65–89% yield within 3 h (**2a–2e**). Cyclopropenes bearing other electron-withdrawing groups such as CN and SO<sub>2</sub>Ph were all suitable substrates and generated the corresponding functionalized bifurans in 63–72% yield (**2g** and **2h**). In addition, cyclopropene derived from ethyl acetoacetate worked well and furnished 2-alkyl substituted bifuran **2f** in 47% yield. Aryl substituted cyclopropenes were more reactive and the



<sup>*a*</sup> Reaction conditions: cyclopropene 1 (0.2 mmol), Pd(OAc)<sub>2</sub> (5 mol%), Cu(OAc)<sub>2</sub> (0.4 mmol), EtOH (0.2 mL), CH<sub>3</sub>CN (1 mL), DMSO (1.4 mmol), 80  $^{\circ}$ C, 3 h. <sup>*b*</sup> At room temperature, 12 h.



Fig. 2 (a) Absorption and fluorescence spectra in DCM. (b) Solution luminescence (2m) (upon irradiation at 365 nm).

bifuran products were obtained in moderate yield even at room temperature (**2g-2o**). This methodology is superior to the existing ones because normal direct C–H/C–H coupling reactions need very high temperature.<sup>7</sup> Remarkably, the halogen groups such as F and Br on the phenyl ring were all tolerated under these mild conditions (**2m**, **2n**). Having halogens on the bifurans makes it possible to couple with other functional groups or chromophores to give larger Pi-extended conjugated functionalized molecules.

The UV/Vis absorption and emission spectra of the bifurans 2a, 2g, 2k and 2m in solution were characterized and are shown in Fig. 2. Both the absorption and emission bands of the aromatic substituted bifurans 2k and 2m are red shifted compared with *n*-butyl group substituted bifurans 2a and 2g. In the fluorescence spectra, 2k and 2m exhibited blue emission at 445 nm, while 2a and 2g exhibited emission at 405 nm. In addition, the fluorescence efficiency of 2k is comparable to the long oligofurans ( $\Phi_f = 0.97$  in DCM). *n*-Butyl substituted bifurans 2a and 2g showed blue emission both at high concentration and in the solid state. By contrast, an aggregation-caused quenching (ACQ) effect was observed for compounds 2k and 2m as they only luminesce in highly dilute solutions (see ESI<sup>†</sup>). These functionalized materials showed great promise as blue emissive materials used as OLEDs.

To gain some insight into the mechanism of the reaction, several control experiments were conducted (Scheme 3). We observed that even when the reaction was conducted at 60 °C, activity was still good. The cyclopropene was consumed in 1 h giving 2a and some trisubstituted furan 4a. When  $Cu(OAc)_2 \cdot H_2O$  was used instead of anhydrous  $Cu(OAc)_2$ , more furan 4a was obtained (92/8 vs. 77/23). When the reaction was carried out at the standard 80 °C, no isomerized furan 4a was observed. If furan 4a was subjected to these standard conditions, bifuran 2a could be produced through



Scheme 3 Control experiments



palladium catalyzed C–H activation, but the reaction was very slow and bifuran **2a** was obtained in only 17% yield in 1 h, and most of the starting **4a** was recovered. These data suggest that there was an equilibrium between the furan palladium intermediate **M** and furan **4a** in the presence of water. In this reaction, the copper–palladium transmetallation is still the major pathway, even though a cycloisomerization to **4a**/palladium catalyzed C–H activation/ dimerization pathway couldn't be ruled out (Scheme 4).

A Tandem Metal Relay Catalysis (TMRC) mechanism is proposed in Scheme 4. Cyclopropene reacts with  $Cu(OAc)_2$ generating the copper carbene intermediate **B**, followed by intramolecular cyclization and elimination of HOAc leading to the vinyl-copper intermediate **D**. Subsequent transmetallation generates the key furan palladium intermediate **M**. The intermediate undergoes disproportionation to afford  $Pd(OAc)_2$  and bifuran palladium **M1**. This then undergoes reductive elimination to generate bifuran 2 and Pd(0), which was oxidized to Pd(II) by  $Cu(OAc)_2$ .

In summary, we have developed a convenient and efficient synthetic methodology toward multifunctionalized bifuran products from cyclopropenes. The mild reaction conditions and high efficiency are the most important features of this formal C–H/ C–H coupling transformation. The Tandem Metal Relay Catalysis (TMRC) mechanism was proposed. The bifuran compounds hold promise for applications as optoelectronic materials. Further work seeking to synthesize and extend bifuran-based Pi-conjugated molecules using this methodolgy and to find applications as organic electronic materials is underway.

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