

Electronic Supplementary Information of

Efficient electrochemiluminescence of a boron-dipyrromethene (BODYPY) dye

Mahdi Hesari,^{a‡} Jia-sheng Lu,^{b,c‡} Suning Wang,^{*b,c} and Zhifeng Ding^{*a}

^a Department of Chemistry, The university of Western Ontario, London, ON N6A 5B7, Canada

^b Department of Chemistry, University of Queen's, Kingston, ON K7L 3N6, Canada

^c Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry, Beijing Institute of Technology, Beijing 100081, P.R. China
zfding@uwo.ca, wangs@chem.queensu.ca

Experimental Details on Electrochemistry and ECL.

The electrochemistry and ECL of the BDY dye were carried out using a 2 mm diameter Pt disc inlaid in a glass sheath as the working electrode (WE), a coiled Pt wire as the counter electrode (CE), and a coiled Pt wire as the quasi-reference electrode (QRE). After each experiment, the electrochemical potential window was calibrated using ferrocene as the internal standard. The redox potential of the ferrocene/ferrocenium (Fc/Fc⁺) couple was taken as 0.342 V vs. SCE.¹ In annihilation ECL studies, a solution containing 0.4 mM BDY and 0.1 M TBAPF₆ as the supporting electrolyte in anhydrous dichloromethane was added to the electrochemical cell with a flat Pyrex window at the bottom for detection of generated ECL. The cell was assembled in a glovebox. For co-reactant studies, 20 mM tri-*n*-propylamine was added to the annihilation solution and the air-tighten cell was also assembled in a drybox.

The cyclic voltammetry was performed on a CHI 610A electrochemical analyzer (CH Instruments, Austin, TX). The general experimental parameters for cyclic voltammograms (CVs) are listed here as follows: 0.000 V initial potential in experimental scale, positive or negative initial scan polarity, 0.1 V s⁻¹ scan rate, 4 sweep segments, 0.001 V sample interval, 2 s quiet time, 1.5 10⁻⁵ AV⁻¹ sensitivity. The ECL-voltage

curves were obtained using the CHI 610A coupled with a photomultiplier tube (PMT, R928, Hamamatsu, Japan) held at 750 V with a high voltage power supply. The ECL was collected by the PMT under the flat Pyrex window at the bottom of the cell was measured as the ECL intensity, and transformed to a voltage signal, using a picoammeter/voltage source (Keithley 6487, Cleveland, OH). The potential, current signals from the electrochemical workstation, and the photocurrent signal from the picoammeter were sent simultaneously through a DAQ board (DAQ 6052E, National Instruments, Austin, TX) to a computer. The data acquisition system was controlled from a custom-made LabVIEW program (ECL_PMT610a.vi, National Instruments, Austin, TX). The photosensitivity on the picoammeter was set manually in order to avoid the saturation.

The ECL spectra were recorded using the Andor Technology program. Similar to the CV experiments, the samples were scanned between their redox potentials. Since the ECL is in NIR region, ECL spectroscopy was conducted on an Acton 2300i spectrograph with two gratings (50 l/mm blazed at 600 nm and 300 l/mm blazed at 700 nm) and an Andor iDUS CCD camera (Model DU401-BR-DD-352). The set of the spectrograph and camera was calibrated using a mercury lamp each time. The accumulation spectra were recorded during two successive potential scan cycles as discussed in each experiment.

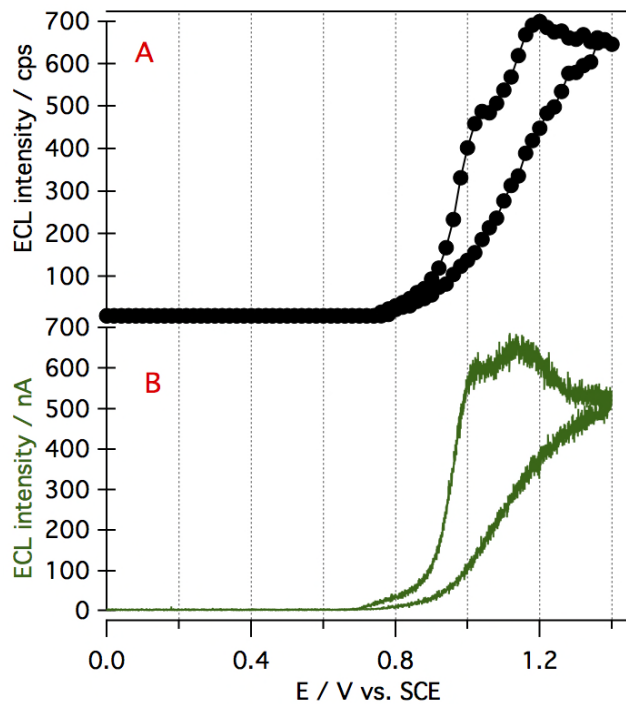


Figure S1. (A) Spooling intensities *versus* the applied potential and (B) ECL-voltage curve of BDY in the presence of 20 mM TPrA at scan rate of 20 mVs^{-1} . The two curves have two maxima at 1.02 and 1.18 V *vs.* SCE that are in agreement with each other.

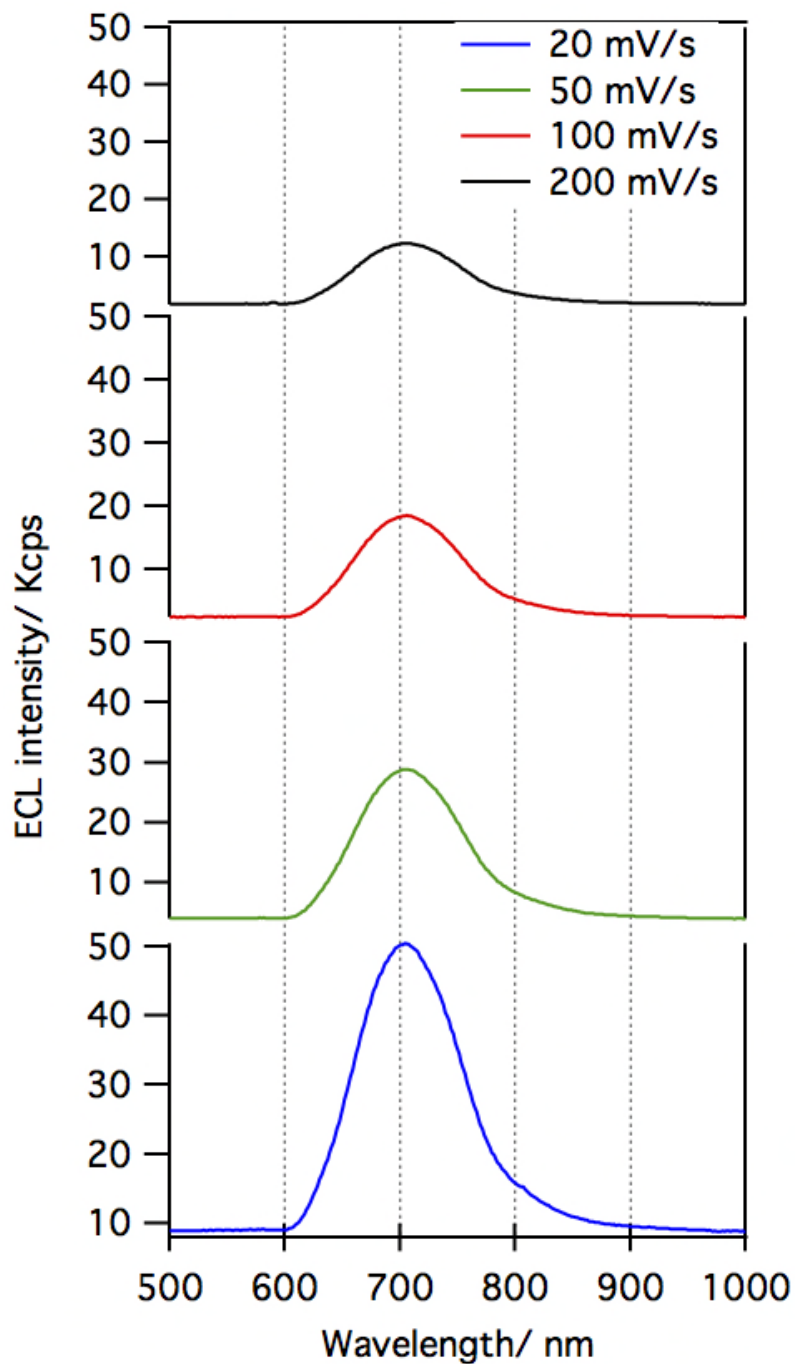


Figure S2. Accumulated spectra of 0.4 mM BDY in CH_2Cl_2 contain 0.1 M TBAPF_6 , at 20, 50, 100, and 200 mVs^{-1} .

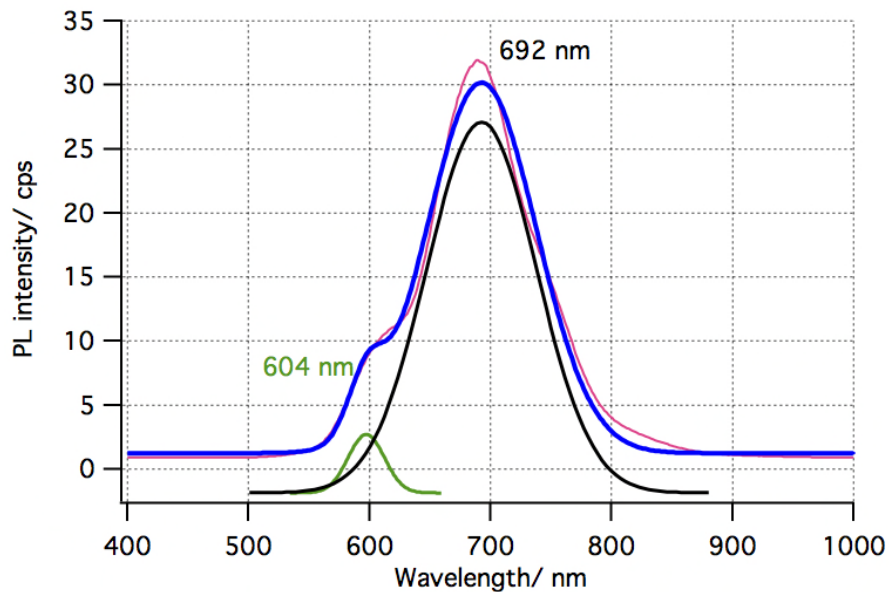


Figure S3. Photoluminescence spectrum and its curve fitting of 0.01 mM BDY dye in CH_2Cl_2 recorded with a BR-DD CCD camera. A 532 nm laser source was used for the excitation.

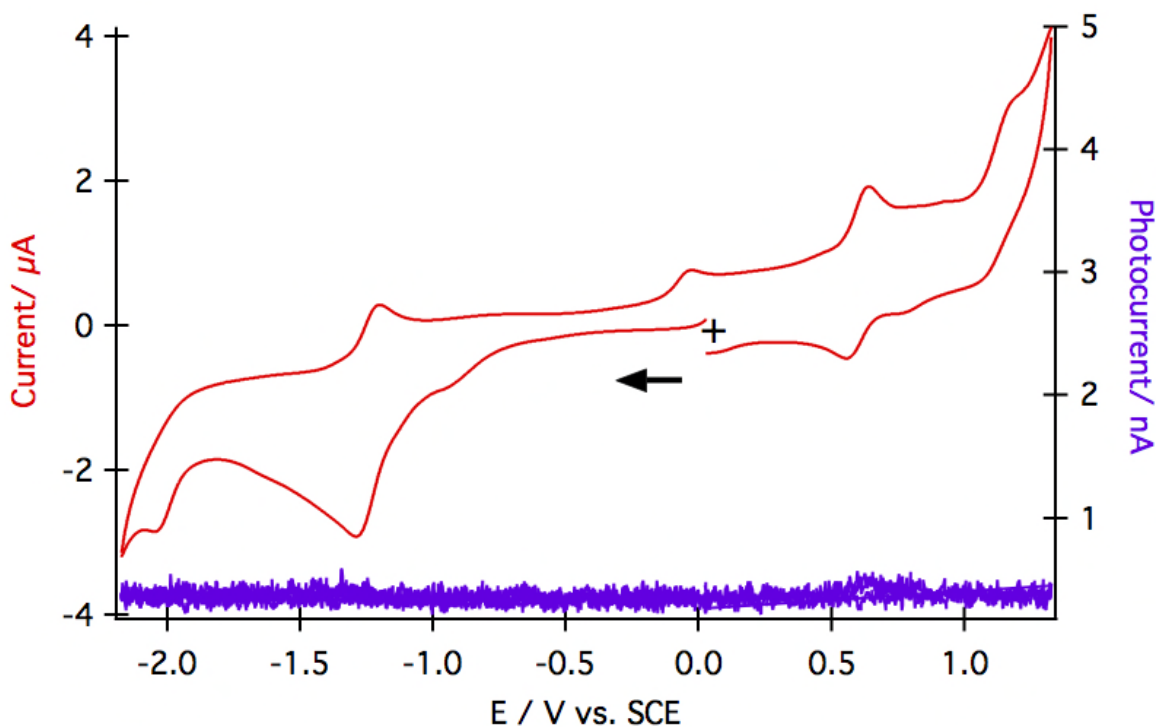


Figure S4. Annihilation ECL-voltage curve of 0.4 mM BDY dye in CH_2Cl_2 containing 0.1 M TBAPF_6 , at 50 mVs^{-1} scan rate. The cross indicates the starting potential. The arrow shows the potential scanning direction.

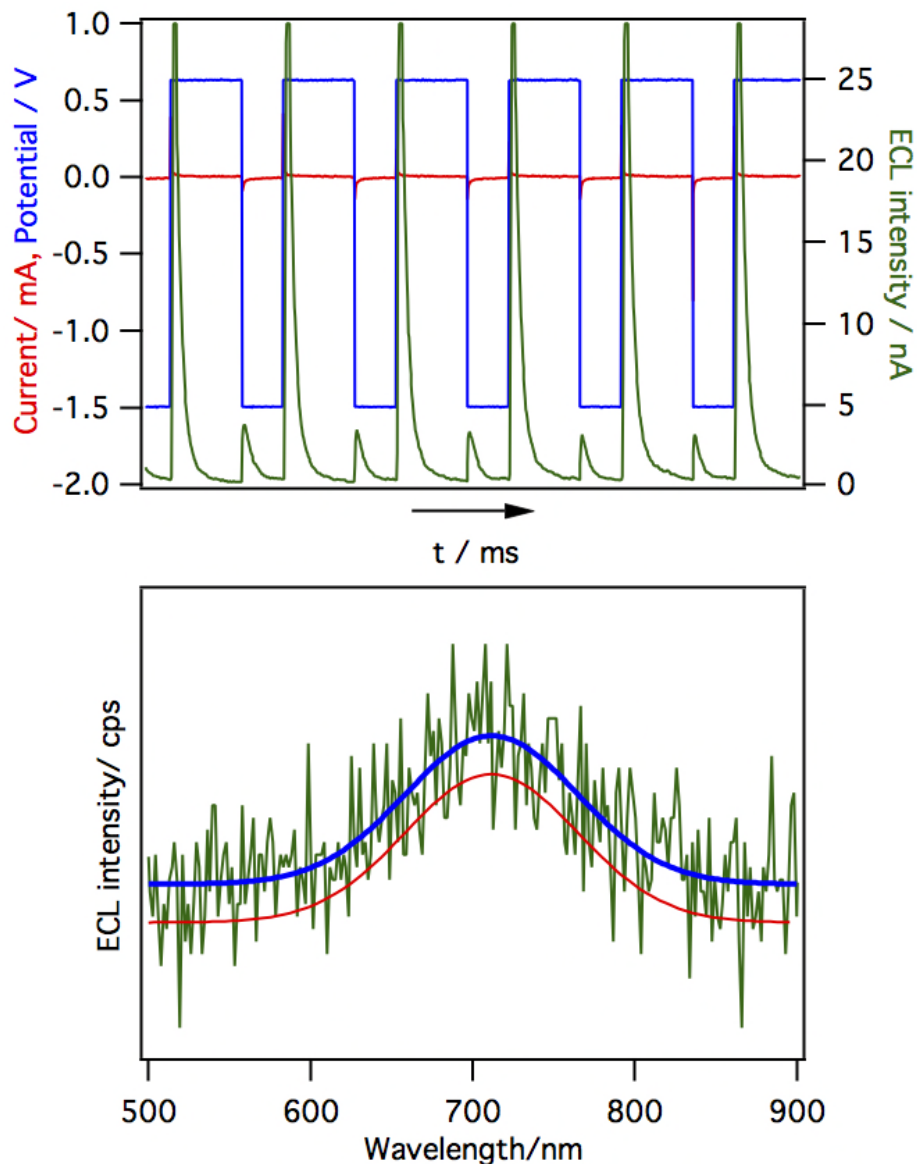


Figure S5. (Top) voltage pulsing between -1.5 and 0.8 V (blue curve) applied to a 0.4 mM BDY solution, corresponding current (red curve) and photocurrent (green curve). (Bottom) The recorded ECL spectrum after the pulsing process for 60 s (green curve), curve-fitting wave (red curve), and the average fitted spectrum (blue).

As an example, ECL efficiency values were calculated by integrating ECL spectrum vs. wavelength and the corresponding cyclic voltammogram vs. time, and comparing the integrated ECL intensities (equivalent to the number photons) and the current values (charges) of the BDY/TPrA samples with those of the reference

Ru(bpy)₃²⁺/TPrA during the ECL experiments. The quantum yield was calculated using the equation below:

$$\Phi_x = 100x \left(\frac{\int_a^b ECL dt}{\int_a^b Current dt} \right)_x / \left(\frac{\int_a^b ECL dt}{\int_a^b Current dt} \right)_{St}$$

where Φ is the quantum yield (%) relative to the Ru(bpy)₃²⁺/TPrA, ECL is the ECL intensity, current is the electrochemical current value, St is the standard (the Ru(bpy)₃²⁺/TPrA) and x is the sample (the BDY/TPrA).

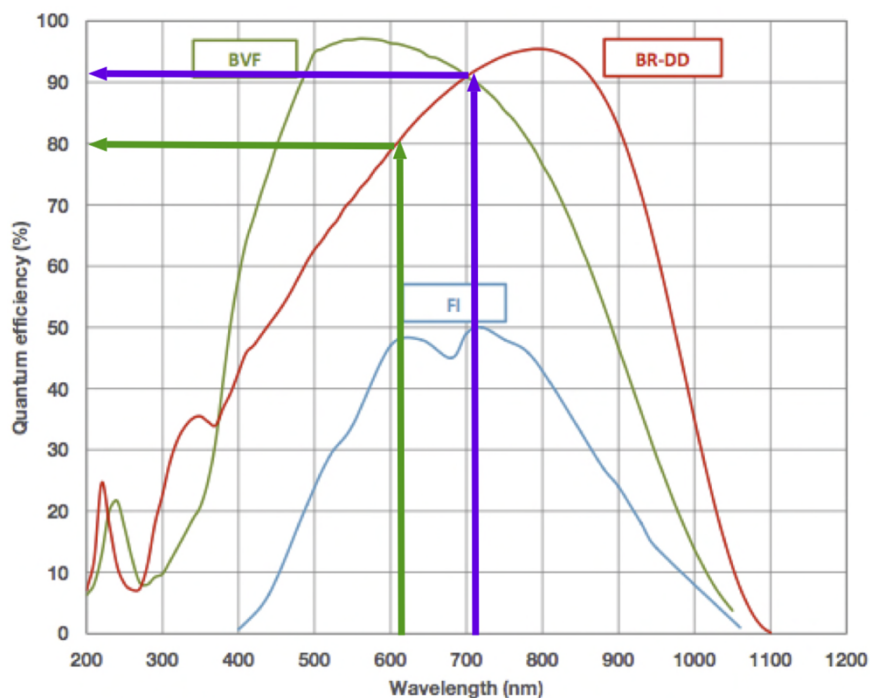


Figure S6. The iDus CCD camera response curve (BR-DD, red). The green and purple arrows indicates the CCD camera's response sensitivity for Ru(bpy)₃²⁺ and BDY dye, respectively.

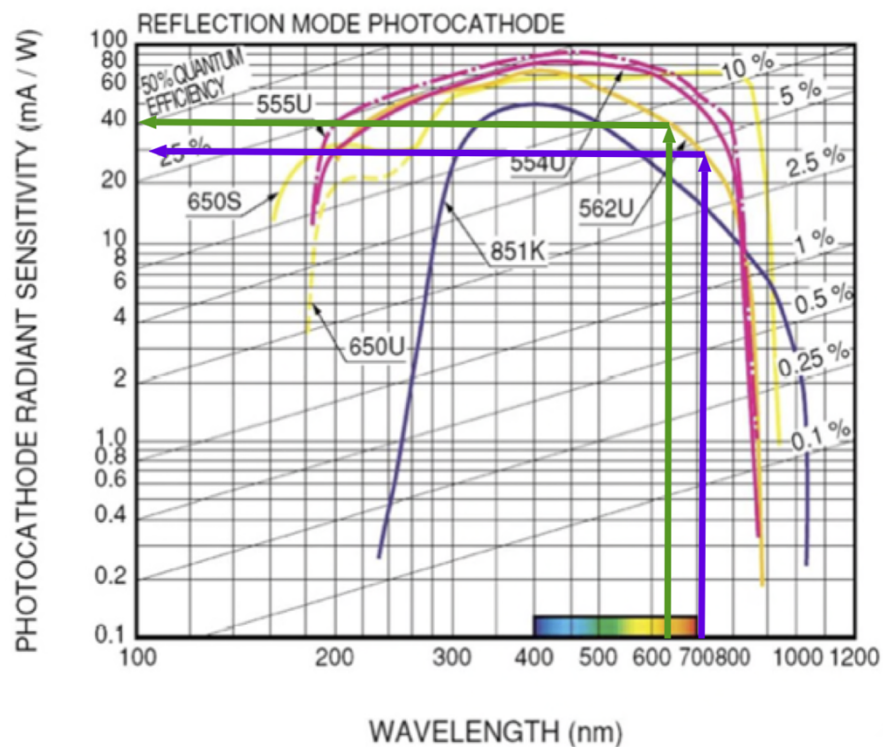
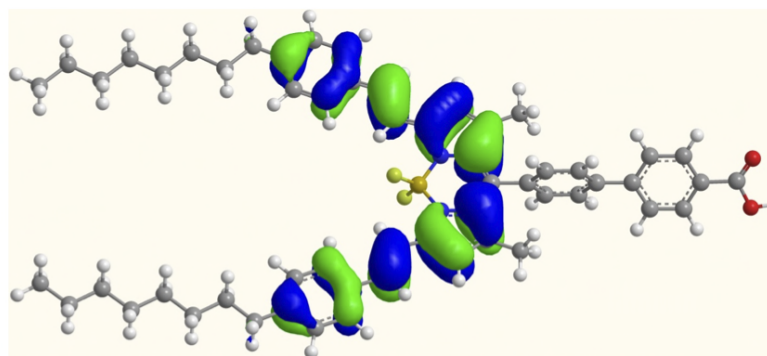
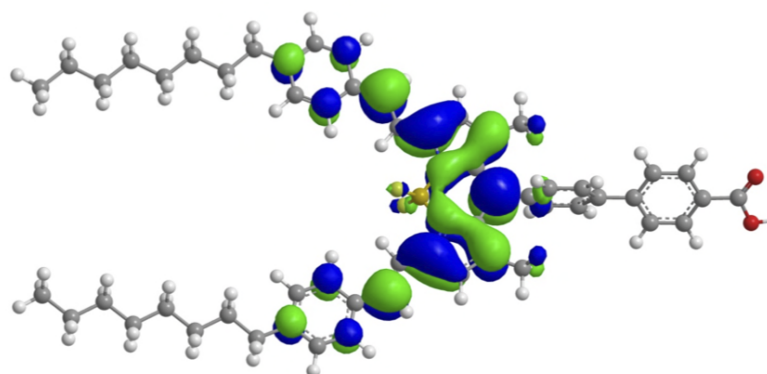


Figure S7. The spectral response curve, 562U for Hamamatsu R928 PMT used in our ECL-voltage curve measurements. The green and purple arrows indicates PMT response sensitivity to the ECL peak wavelengths of $\text{Ru}(\text{bpy})_3^{2+}$ and BDY dye, respectively.



HOMO



LUMO

Figure S8. HOMO and LUMO orbitals of the BDY dye.²

References

1. A. B. Nepomnyashchii, M. Bröring, J. Ahrens and A. J. Bard, *J. Am. Chem. Soc.*, 2011, **133**, 8633-8645.
2. J.-s. Lu, H. Fu, Y. Zhang, Z. J. Jakubek, Y. Tao and S. Wang, *Angew. Chem. Int. Ed.*, 2011, **50**, 11658-11662.