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Title: Transition-Metal-free Oxidative C(sp2)-H Hydroxylation of Terpyridines: A HOMO-Raising Strategy for the Construction of A Super-Stable Novel Terpyridine Chromphores

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Transition-Metal-free Oxidative C(sp^2)-H Hydroxylation of Terpyridines: A HOMO-Raising Strategy for the Construction of A Novel Super-Stable Terpyridine Chromophores

Jiang-Bo Huang, Xing-Feng Bai, Li Li, Zhan-Jiang Zheng, Zheng Xu*, Yu-Ming Cui, Jian Cao, and Li-Wen Xu*

((optional))

Abstract: *Direct functionalization of terpyridines is an increasingly important topic in the field of dyes and catalysis as well as supramolecular chemistry, but its synthesis and transformation is usually challenging. In this manuscript, we reported a HOMO-raising strategy for the construction of a super-stable novel terpyridine chromophores, in which the selective oxidation of terpyridines at its 3-position was determined successfully to the synthesis of phenol-functionalization of terpyridines (TPyOHs) bearing a hydrogen bonding group. The corresponding TPyOHs displayed strong aggregation-induced emission and exhibited highly selective and visual detection of Zn(II) cation with a record green terpyridine-based luminophore with nanomolar sensitivity (125 nM).*

2,2':6',2''-Terpyridines consist of three linked pyridine, could be synthesized easily from commercially available starting materials, which provide three strong *N*-binding centers for coordination of metal ion to form stable metal complex. Now, the construction of terpyridine-containing architectures has great importance in chemistry, materials science, and biology owing to the ability of coordination-driven self-assembly and ranging from mononuclear metal-coordinated compounds to higher-order domain structures, for the potentially significant applications in photoelectronics, catalysis, sensors, functional materials, and so on.[1] The planar structure of terpyridine is a unique hemispherical molecule containing three heterocyclic nitrogen centers on the backbone, and this rigid and stable structural motif and its coordinated chemistry have attracted extensive attention in the past decades.[2] Especially in the past years, there has been considerable research work conducted on octahedral terpyridine-based transition metal complexes featured with capability of fine-tuning of corresponding electrochemical and optical properties as well as transition-metal-complexed molecular machine prototypes.[3,4] However, by and large, functionalized terpyridines or its complexes have been underutilized due to their limited accessibility, difficult introduction of functional substituents because of the super-stable terpyridine rings, and low chemoselectivity and the generally poor yields of multi-step group-transformations.[5] On the other hand, although many compounds have been reported as good sensors for metal cations, only a limited number of terpyridines could be applied as fluorescent probes. Notably, there are no reports on AIE-active terpyridine compounds without any substituted groups because their special structures without the commonly known AIE moieties, such as silole, anthracene, tetraphenyl ethylene, and carbazole.[6] Therefore, the design and functionalization of terpyridines which can be used in selective enhancement of optical and physical properties especially work as a fluorescent probe, is highly desirable. Accordingly, our goal is to develop a one-step synthesis of a functionalized terpyridine ligand that had the potential to be a new fluorescent probe for metal ions.

It is well known that reductive PET (photoinduced electron transfer) is used frequently in the design and application of BODIPY-based sensors, in which the BODIPY fluorophore acts as the electron acceptor and the chelator (for example, the amine group) is the electron donor.[7] In addition, the most important feature of π-conjugated fluorophore compounds with electron-accepting (A) and electron-donating (D) groups is the intramolecular charge-transfer (ICT), which resulted into strong emission, photoabsorption, electroluminescence, and other optical properties, making them promising candidate for two-photon fluorescent probes and OLED.[8] In general, for both reductive PET and ICT systems, the HOMO (highest occupied molecular orbital) of the fluorophore provides a key information for the design a novel fluorescent sensor upon photo-excitation. Thus we hypothesized that the introduction of a hydroxyl group to the terpyridine rings would be a simple and direct strategy to promote HOMO level of terpyridines. To test the hypothesis of hydroxyl group-raising HOMO of general terpyridines, theoretical calculations of molecular orbitals for all the possibly hydroxylated terpyridines were also performed using Gaussian 09 software package (Figure 1) [9]. It is noteworthy that the electron density of the HOMO of only the hydroxyl-substituted terpyridine **T5** and **T6** is spread over the donor aryl rings, while the HOMO of its terpyridine precursor and other hydroxylated terpyridines is mainly localized on the three pyridine units or phenyl ring. Encouraged by our hypothesis and corresponding calculation, we paid much attention to the hydroxylated functionalization of general terpyridines to the synthesis of terpyridine **T5** with the highest level of HOMO showed in Figure

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1. It should be noted that, no reported effort has been devoted to replacing C-H by C-OH bond via oxidation of terpyridines, and most methods for the synthesis of functional terpyridines are fulfilled on the modification of backbone of *N*-para-position that inherited from the building block of starting aldehyde. Herein, we report our finding on the unprecedented functionalization of terpyridines via strong base-mediated air oxidation reaction. And our results show that the corresponding terpyridine derivatives, simplified as TPyOHs, exhibit excellent Zn(II) cation binding selectivity over other structurally analogues terpyridines without *ortho*-OH-functional groups.

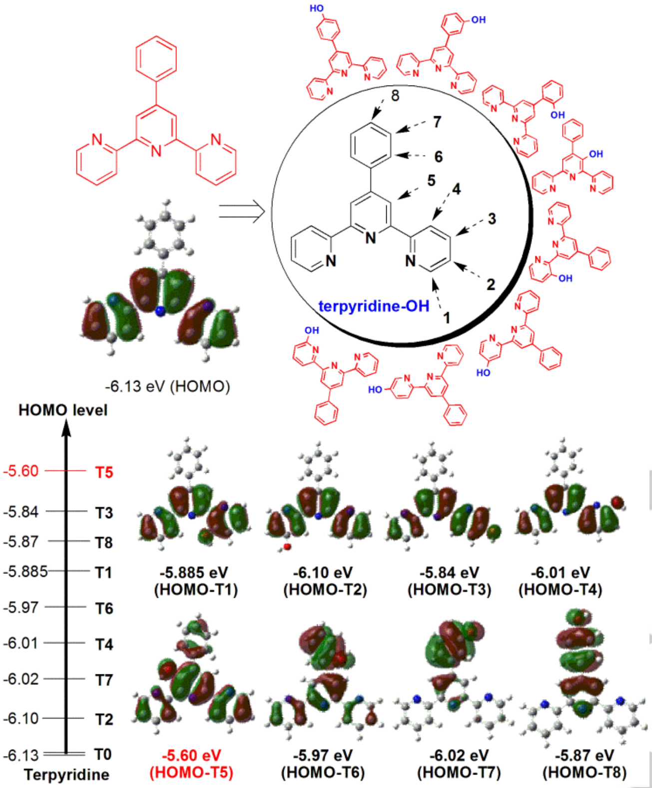
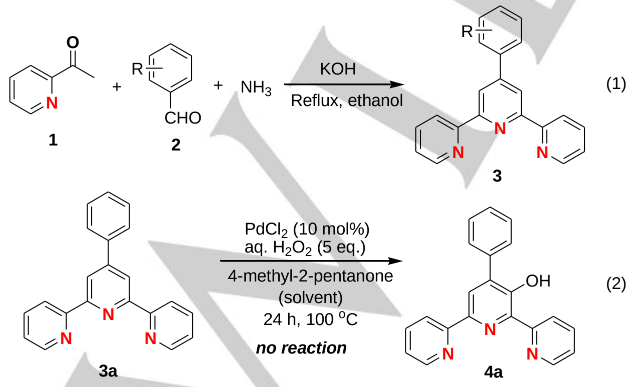
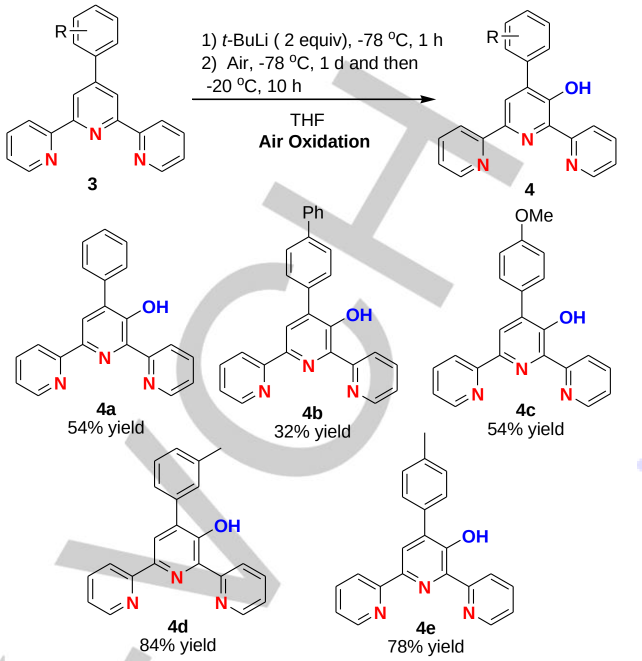


Figure 1. Hydroxyl group-raising HOMO level of general 2,2':6',2''-terpyridine molecules: A motivation for the design of a novel HOMO-raising terpyridine-conjugated–donor-acceptor (TCDA) chromophore.



Scheme 1. Classic method for the synthesis of general terpyridines **3** (equation 1) and the initial and unsuccessful exploring of palladium-catalyzed hydroxylation of terpyridine **3a** (equation 2).



Scheme 2. Substrate scope of strong base (*t*-BuLi) -promoted air oxidation of 2,2':6',2''-terpyridines.

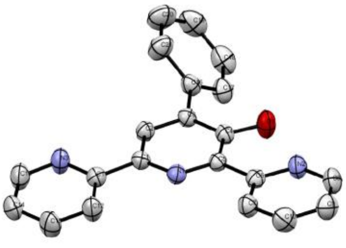


Figure 2. The crystal structure of 4-phenyl-2,6-di(pyridin-2-yl)pyridin-3-ol **4a** (CCDC 1520339). H atoms have been omitted for clarity.

Initially, we found that the metal catalysts, especially palladium and copper complex have no enough ability to activate C-H bond on the aromatic ring of 2,2':6',2''-terpyridines to occur C-H hydroxylation under the reported reaction conditions[10] (Scheme 1). Due to the high stability of terpyridines, we felt the need to establish a facile strategy aiming at the straightforward C-H functionalization on the pyridine rings of terpyridines. Then on the basis of our previous work on lithium chemistry,[11] we hypothesized that *ortho*- lithiation and subsequent hydroxylation could be a possible strategy for the facile construction of structurally defined terpyridine derivatives bearing new OH-functional groups. In order to improve the ability of lithiation of terpyridine, we used *t*-BuLi as a strong base to initiate the lithiation/air oxidation. Fortunately, the dehydrogenative oxidation occurred under the air atmosphere after lithiation of terpyridine with *t*-BuLi. The air oxidation of terpyridine **3a** resulted in the formation of desired OH-functionalized terpyridine **4a** in promising yield (see Table S1 of Supporting Information). Encouraged by this preliminary and unprecedented finding, we

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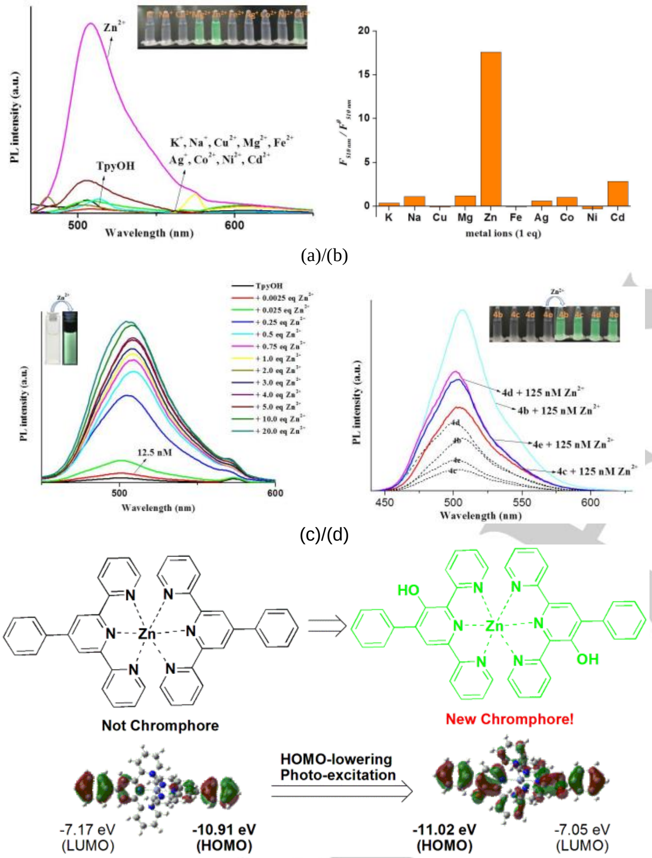
continued to optimize the reaction conditions for the high-yield synthesis of OH-functionalized terpyridines in the *t*-BuLi - promoted air oxidation reaction of terpyridine **3a**. Fortunately, under the optimized reaction conditions, the lithiation-oxidation of terpyridine **3a** resulted into the desired product (TPyOH **4a**) in 54% isolated yield. The obtained novel OH-functionalized terpyridine **4a** was characterized by NMR, mass spectroscopy, and confirmed by X-ray crystallography (Figure 2).

We further briefly examined the substrate scope of this novel air oxidation reaction of terpyridines under the optimized reaction conditions. As shown in Scheme 2, versatile products **4a**-**4e** could be achieved in moderate to good yields (up to 84% isolated yield). The facile one-step oxidation of terpyridines at 3-position to TPyOHs **4a**-**4e** provided an unprecedented method for the functionalization of general terpyridines as well as newly designed fluorescence probe.



(a)/(b)

(c)/(d)

Figure 3. (a) Fluorescence emission spectrum of TPyOH/cation mixtures (5 μM, 1:1) in EtOH/water (99:1) solution (λex = 430 nm). (b) Fluorescence enhancement $F_{510\,nm}/F^{0}_{510\,nm}$ ($F^{0}_{510\,nm}$:TpyOH. $F_{510\,nm}$: TpyOH with metal cations.). (c) Fluorescence emission spectra of TpyOH (5 μM, EtOH/water = 99 /1) in the presence of Zn^{2+} at various concentrations including 0, 0.0025, 0.025, 0.25, 0.5, 0.75, 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, and 20.0 equiv (λex = 430 nm). (d) Fluorescence emission spectra of other TpyOHs (**4b**, **4c**, **4d**, and **4e**) (5 μM, EtOH/water = 99/1) in the presence of Zn^{2+} (125 nM), λex = 430 nm.

While a number of recognition-based multitopic receptors have been studied in the field of supramolecular chemistry, OH-functionalized terpyridines at 3'-postion of center pyridine unit for binding of metal cations and hydrogen bonding activation have never reported. Considering that the terpyridine core (2,2':6',2''-terpyridine) has been extensively used as a metal ion receptors in coordination chemistry and fluorescent sensor,[2,3,12] we initially tested the chemoselective and fluorescent sensing ability of 4-phenyl-2,6-di(pyridin-2-yl)pyridin-3-ol (TPyOH **4a**) to detect various metal ions, such as Cu^{2+}, Mg^{2+}, K^{+}, Na^{+}, Fe^{2+}, Co^{2+}, Ag^{+}, Ni^{2+}, Cd^{2+}. As seen from Figure 3a and 3b, the TPyOH **4a** displayed obvious fluorescent enhancement toward Zn^{2+}, whereas most of ions evaluated in this work caused fluorescent quenching of TPyOH **4a**. To further illustrate the quantitative sensing of TPyOH (5 μM) toward Zn^{2+}, fluorescent titrations were carried out carefully. As shown in Figure 3c, the intensity of the fluorescent peak of TPyOH **4a** at 510 nm was remarkably increased upon the addition of Zn^{2+} (0-20 eq.). Similarly, the addition of Zn^{2+} to other TPyOHs (**4b**-**4e**) was also observed as fluorescent enhancement at nanomolar level of concentration (125 nM, Figure 3d). The above results suggested that when TPyOH **4a** was bonded with Zn^{2+}, a novel green and stable luminophore was formed, and the electron transfer from the phenol electron donor to the terpyridine core became more favorable and finally caused fluorescence enhancement in the presence of Zn^{2+} ion, which is largely different from that of unmodified terpyridines **3** (*see* ESI, Figure S8).

As shown in Figure 1, the incorporation of a OH-functional group at the 3'-position of a terpyridine unit possibly has the pronounced effect on electronic and physical properties of terpyridine-based metal complex or intermolecular interaction. The electron density diagrams for LUMO and HOMO orbitals of TPyOH **4a** as well as the Zn-TPyOH (**4a**) complex were provided in Table S2. It is noteworthy that the electron density of the HOMO of the TPyOH **4a** was spread over the donor aryl rings and the LUMO predominantly distributed dispersively along the two pyridine rings. Although the electron density of the LUMO of terpyridine **3a** without phenol group at 3-position was also mainly localized on the acceptor pyridine rings, different from that of **4a**, its HOMO was mainly localized on the three pyridine units. The calculations showed that the lowest energy absorption band of **4a** represented the HOMO→LUMO transition which resulted into the strong fluorescent sensing ability of **4a** to zinc ion and was probably assigned to a combination of intramolecular charge-transfer and π-π* excitation. Similarly, the HOMO/LUMO orbitals of Zn-**3a** and Zn-**4a** were also reported in Table 1, and it is worth noting that the LUMO value of the Zn-**4a** complex is the lowest in comparison to that of Zn-**3a**. This feature indicates that the energies of orbitals could be affected by phenol unit largely.

We further investigated the applicability of aggregation-induced emission (AIE)[13,14] in the two system of TPyOH **4a** and Zn-TPyOH (**4a**) complex respectively because of the strong π-π interaction aroused from planar terpyridine molecular unit and possible hydrogen bonding of phenol group on the TPyOH (Figure 4). The corresponding emission spectra of TPyOH **4a** in aqueous THF with different THF/water ratios are shown in Figure 5. As expected, fluorescence emission enhancement from pure THF solution to THF/water solutions of corresponding TPyOH **4a** and Zn-TPyOH (**4a**) respectively were observed simultaneously. Notably, luminescence was significantly enhanced for approximately 20:80 (v/v) and 10:90 (v/v) THF/water mixtures for TPyOH **4a** and Zn-TPyOH (**4a**).

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Especially, almost no PL signs were recorded for TPyOH **4a** in the pure THF, but the PL value increased to about 1100 in 10:90 (v/v) THF/water (Figure 5a). The fluorescence emission enhancement was induced by the aggregation of TPyOH molecules, thus suggesting that such TPyOH compounds and its zinc complex are AIE active. Our experimental studies revealed that the introduction of phenol group on the 3-position of terpyridines dramatically increased the fluorescent ability because of their molecular π-π packing structures assisted by intermolecular hydrogen bonding activation (Figure 4).

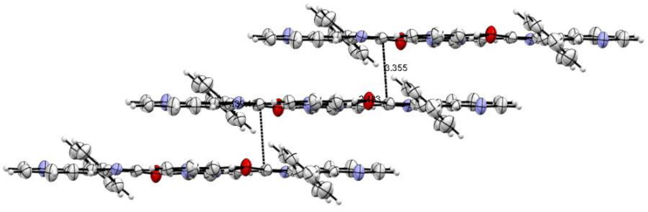
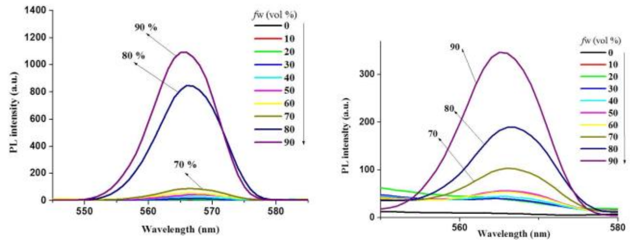


Figure 4. Packing diagrams of TPyOH **4a**.



(a)/(b)

Figure 5. (a) Fluorescence emission spectra of TpyOH in THF–water mixtures (*f*w = 0 and 90%). (b) Fluorescence emission spectra of TpyOH /Zn^{2+} (5 μM, 1:1) mixture in THF–water mixtures (*f*w = 0 and 90%). λex = 280 nm, λes = 545 nm.

In conclusion, on the basis of the hypothesis that the introduction of a hydroxyl group to the terpyridine rings would be a simple and direct strategy to promote HOMO level of terpyridines, we have successfully developed a strong base (*t*-BuLi) -assisted air oxidation of simple terpyridine, in which a series of novel terpyridine molecules (simplified as TPyOHs) bearing a phenol group at 3-position were prepared in good yields. In addition, it was found that these TPyOHs displayed strong fluorescence in the presence of nanomolar zinc ions. And the TPyOHs **4** displayed strong aggregation-induced emission in THF/water solution. These novel terpyridine derivatives, which display high fluorescence intensity and visual Zn^{2+} ion recognition achieved here, are desirable for various applications such as fluorescent sensor and organic luminescence devices.

Keywords: Selective oxidation • terpyridine • molecular recognition • aggregation-induced emission • lithium

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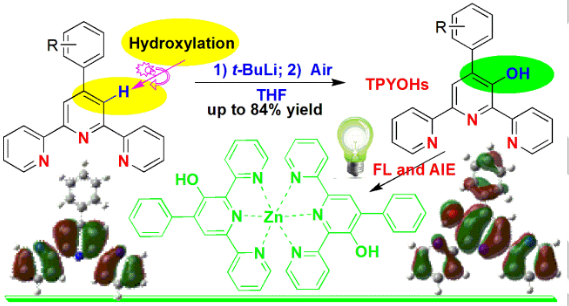
Layout 1:

COMMUNICATION

A HOMO-Raising Strategy: It is the first example to reveal clearly that a new family of terpyridine molecules bearing a phenol group at 3-position (simplified as TPyOHs) could be prepared via *t*-BuLi promoted air oxidation of simple terpyridines, which provide a high useful fluorescent probe to zinc cation and AIE active molecules and Zn complex as a green luminophore.



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Transition-Metal-free Oxidative C(sp^2)-H Hydroxylation of Terpyridines: A HOMO-Raising Strategy for the Construction of A Novel Super-Stable Terpyridine Chromophores

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