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A Designed TEMPO-derivate Catalyst with Switchable Signals of EPR and Photoluminescence: Application in the Mechanism of Alcohol Oxidation

Lu Yin,^[a] Jiaxiang Zhang,^[a] Jia Yao,^[a] and Haoran Li *^[a,b]

Abstract: Construction the in situ, real-time monitoring methodology for chemical changes, especially in the mechanism of oxidation, has long been regarded as a significant and challenging concern. Herein, **TEMPO-mediated** we designed and synthesized а alkynylplatinum(II) terpyridine complex with switchable activity in photoluminescence and EPR (Electron Paramagnetic Resonance) spectra. This complex of alkynylplatinum(II) terpyridine-TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] is paramagnetic, while the in situ formed alkynylplatinum(II) terpyridine-TEMPOH is diamagnetic, so that concentration changes of TEMPO/ TEMPOH species were obtained successfully by photoluminescence and EPR spectra in an operando way. As a model example, we investigated the mechanism of alcohol oxidation mediated by TEMPO/ bis(acetoxy)iodo]benzene (BAIB). It was found that, with the consumption of co-oxidant (BAIB), the concentration and conformation of catalyst (TEMPO) were changed gradually, and the vital role of catalyst and co-oxidant in the benzyl alcohol oxidation was clearly showed by photoluminescence and EPR spectroscopies. On the basis of these observations, we suggested an effective methodology to study the mechanism of chemical reaction, which is promising for further practical applications in analytical or environmental issues.

Introduction

TEMPO-mediated oxidations of alcohols attract much attention.^[1] Those pathway are facilitated by the transition metal or metal-free stoichiometric oxidants,^[2, 3] to undergo two-electron redox steps. Of the particular contribution in this field is the use of TEMPO and copper as oxidants pioneered by the groups of Sheldon and Stahl.^[4] Currently available set-ups for catalyst characterization and reaction monitoring range all the way,^[5] whereas the intermittent sampling methods may lose part of information more or less, so real-time and in situ methods for studying the working catalyst and interpretation of reaction mechanism are necessary. In recent years, the UV, infrared, and Raman spectroscopy were most common in application of *in situ* oxidation,^[6] but *in situ* EPR and fluorescence spectra are relatively rare. Pioneering work has been done by the group of

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Bruckner who presented commendably the first three coupled operando spectroscopies setup for mechanistic studies of copper/TEMPO-catalyzed alcohol oxidation. They have directly detected the redox reaction of TEMPO and Cu^I/Cu^{II}, and postulated that TEMPO could stabilize the copper complex-TEMPO intermediate.^[7] However, in some cases, the TEMPOH species are also key intermediates in the recycle process, the detection of TEMPOH species have not been concerned much. If we developed a method to take notice of TEMPO species and TEMPOH species at the same time, we could trace more details about TEMPO-mediated reaction.

As we know, TEMPO is paramagnetic species which can be detected by EPR spectrum, whereas TEMPOH belongs to diamagnetic species, which can be detected by other spectrum, fluorescence spectrum, for example. The fluorescence spectrum has the advantages of high sensitivity, chemical specificity, selectivity and continuity in studying catalysis,^[8] and the spectroscopy of EPR is powerful in studying solid catalysts and molecular interactions in situ studies,^[9] specifically in detecting paramagnetic species containing unpaired electrons. Thus, the fluorescence and EPR spectroscopies are complementary each other, but signals of the two spectra are not likely to occur in the meantime. For purpose of obtaining a realistic situation of the working catalytic reaction without sacrificing required reaction integration of conditions. simultaneous two in situ spectroscopies to monitor the composition of product is becoming more advantageous.^[10] If a TEMPO-mediated catalyst with switchable responses to EPR and photoluminescence spectroscopy was synthesized, the status of TEMPO and TEMPOH species could be achieved easily in a reaction.

Based on knowledge of structure-reactivity relationships of catalysts, we have rationally designed and synthesized a novel bifunctional molecular probe with fluorescence and EPR properties, $[Pt(terpy-TEMPO)(C=CPh)](PF_6)$, (Complex 1, terpy = 2,2':6',2"-terpyridine), which is also an appropriate TEMPOcontaining platinum terpyridine complex catalyst. As alcohol was oxidized by TEMPO, accordingly, aldehyde and TEMPOH were formed. Subsequently, the TEMPOH was converted to TEMPO again by the co-oxidant of BAIB which was mole equivalent to alcohol. So the change of TEMPO/TEMPOH signal could reflect the process of substrate oxidation in real time. In addition, the different molecular states of Complex 1 can be detected by different spectroscopic methods during the catalytic reaction, to show directly the real-time state of the reaction process. Then we revisited the well-known alcohol oxidation by using Complex 1 instead of TEMPO in along with BAIB. In this case, benzyl alcohol oxidation was catalyzed efficiently by Complex 1 as TEMPO did. Moreover, it could act excellently as an EPR/fluorescence bi-functional probe in this reaction, due to the entirely different behavior of TEMPO style (paramagnetic species) and in situ formation of TEMPOH style (diamagnetic species) from Complex 1.

Thus, a method of coupled fluorescence/EPR was established to monitor directly the changes of chemical reaction. Via operando combining the fluorescence and EPR spectra, we could obtain an efficient method for the studying of the catalytic mechanism.

Results and Discussion

Photophysical Studies of the Complexes

Platinum terpyridine complexes were prepared via a modified ligand-chelation and ion-exchange methods, as illustrated in Scheme 1. These complexes with different substituent in terpyridine ligand, terpy, terpy-TEMPO or terpy-TEMPOH, were named as [Pt(terpy)(C=CPh)](PF_6), Complex 2; [Pt(terpy-TEMPO)(C=CPh)](PF_6), Complex 1; [Pt(terpy-TEMPOH)(C=CPh)](PF_6), Complex 1', respectively.

Complex 1 was prepared according to the method of Burstall et al^[11] and Lippard et al^[12] as modified by our group in synthesis of Platinum terpyridine-TEMPO complex.^[13] Complex 2, $[Pt(terpy)(C=CPh)](PF_6)$, without TEMPO was gained by the analogous copper-catalyzed method.

Generally speaking, rich photophysical properties were showed by alkynylplatinum(II) terpyridine complexes,^[14] so it was unambiguous that Complex 1 displayed typical π - π *, LLCT and MLCT transitions (Figure 1 A). The transitions of Complex 1 were similar to Complex 2 in which there was no substituent of TEMPO. Therefore, the TEMPO radical introduced to the terpyridine did not affect the electron transition of the alkynylplatinum(II) terpyridine. Upon subsequent adding of ascorbic acid into the DMF solution of Complex 1(the experimental details see supporting information), the complex gradually turned into diamagnetic species Complex 1' (Figure 1 B) leading to the switch off of the EPR signals, meanwhile, luminescence emission switched on. It was visualized that the EPR signal lost, and at the same time the luminescence appeared (Figure 1 B, C), which was reversible upon adding BAIB (Figure S4). Furthermore, the emission property of Complex 1' was analogous to Complex 2 to show a maximum emission wavelength at 566 nm, verified by the similar fluorescence spectra of the two complexes (Figure 1 B). Therefore, Complex 1 shows obvious EPR signals and potential emission signals. Moreover, these properties are very helpful in the study of reaction mechanism.



Scheme 1. Synthetic routes and structures of alkynylplatinum(II) terpyridyl Complexes 1, 1' and 2.

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Figure 1. UV-Vis spectra, photoluminescence spectra and EPR spectra of complexes. A) curves of Complex 1(black) and 2 (red) was UV-Vis spectra, B) curves of Complex 2 (blue), Complex 1 (cyan) and Complex 1' (green) were photoluminescence spectra, C) and curves of TEMPO (violet), Complex 1 (orange), and Complex 1'(pink) were EPR spectra, all in the DMF at the concentration of 1×10⁻⁴ mol. L⁻¹, rt.

Coupled Operando Spectroscopic Studies of Complex 1 in the Catalytic Reaction

During the alcohol oxidation, Complex 1 was explored to TEMPO-mediated catalyst, as well as the bi-functional probe with switchable signal of EPR and photoluminescence. So fluorescence emission and EPR spectroscopic studies were performed to visualize the catalyst species of TEMPO/TEMPOH. Piancatelli and co-workers described an effective BAIB/TEMPO-catalyzed oxidation of alcohols.^[15] Thereby, the famous oxidation of benzyl alcohol to benzaldehyde was revisited to demonstrate the advantages in studying mechanism by using Complex 1 instead of TEMPO in along with BAIB as a co-oxidant, and the mechanism of benzyl alcohol oxidation was also discussed.



Under the standard conditions, Complex 1 exhibited a high selectivity (99%) and excellent efficiency in oxidation of benzyl alcohol to benzaldehyde (detected by GC, Figure S8).

Through the combination of EPR and photoluminescence techniques, Complex 1 could manifest actively EPR signal as well as luminescence signal in the oxidation system. Here the EPR signal of Complex 1 showed broadened and decreased but the emission band appeared with time at maximum wavelength 566 nm after adding benzyl alcohol (abbreviated to BzOH), indicating the oxidation of Complex 1 (TEMPO style) to Complex 1' (TEMPOH style), as showed in Figure 1 B, C. In the meantime, the oxidation reaction was also evidenced from the corresponding GC analysis (Figure S8), in which benzaldehyde (abbreviated to BA) increased and benzyl alcohol decreased

with time. As a co-oxidant, BAIB experienced hydrogen abstraction from TEMPOH, forming PhI and AcOH.





The reaction rate of catalyst can be observed directly with the aid of Complex 1 which produced the EPR signal as well as the luminescence signal. As Figure 2 showed obviously, there were three stages in the whole reaction. The first stage (Figure 2, 0-15 min), the concentrations of Complex 1 and 1' kept steady, while benzyl alcohol was converted by the oxoammonium salt (TEMPO⁺ style) which is commonly known as a kind of stronger oxidant compare to the corresponding radical style in oxidation of alcohols.^[16,17] Our control experiments showed clearly that

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TEMPO or BAIB alone could not oxidize benzyl alcohol efficiently (Table S1).

In the second stage (Figure 2, 15-45 min), the steady state was destroyed, where the photoluminescence intensity enhanced, and EPR intensity fell off.

In the third stage (Figure 2, 45-65 min), the concentrations of TEMPO and TEMPOH species were in another steady state: the EPR signal of was low intensity, and the photoluminescence signal of was relative high intensity.

In general, the oxidation of the alcohols was closely related to the states of catalysts, thus more information on the oxidation mechanism of the substrate could be obtained through the detailed changes of the catalysts.



Scheme 2. The process of acid-catalysed disproportionation of nitroxyl radical [1], alcohol oxidation of BzOH [2], and reduction reaction of TEMPOH species [3].

New Insights on Transformation and Termination States of TEMPO Species in the Benzyl Alcohol Oxidation by Complex 1/BAIB System

The strategies of coupled operando spectra make the possibility to gain insight into the vital changes of TEMPO/TEMPOH and states of termination for working catalysts in order to know a more comprehensive mechanism in the alcohol oxidation. There were also three key processes in the benzyl alcohol oxidation by BAIB/TEMPO system. Firstly, Since no TEMPO⁺ appeared at the beginning of the alcohol oxidation reaction, it was formed by disproportionation of the nitroxyl radical (Scheme 2, disproportionation process [1]).^[18] Secondly, the TEMPO⁺ species oxidized effectively alcohol, forming aldehyde and TEMPOH species (Scheme 2, alcohol oxidation process [2]). Thirdly, In the presence of co-oxidant (BAIB), TEMPO was regenerated from TEMPOH, and BAIB was reduced to PhI and AcOH (Scheme 2, regeneration reaction process [3]).

Based on the above results, we present an integrated reaction mechanism (Scheme 3). One mole of TEMPO⁺ species (Complex 3) and one mole of TEMPOH species (evidenced by the emission spectrum, Figure 2) were formed from the disproportionation of two moles of TEMPO species (Complex 1). Then benzyl alcohol was oxidized to benzaldehyde by the *in*

situ-formed TEMPO⁺ species, and at the same time, TEMPO⁺ was reduced to another mole of TEMPOH. Two moles of TEMPOH may be deprotonated by BAIB^[19], BAIB accordingly release the AcOH and PhI, and TEMPOH was turned to Complex 1 (evidenced by the EPR spectrum).



Scheme 3. Proposed reaction pathway for alcohols oxidation by BAIB and Complex 1.

In accordance with the established calibration curves (eqs.1 and 2, methods of measurement were in supporting information) between the concentration and intensity in the region of 0.1-1.0 mol. L⁻¹, the intensities showed in Figure 2 were transformed to corresponding concentrations in Figure 3, and the equations of time-resolved density were fitted as eqs. (3) and (4). Where y values referred to the intensity of EPR signal of Complex 1 in eq. (1) or emission signal intensity of Complex 2 in eq. (2). C₁, C₁[,] and C₂ referred to the concentration of Complex 1, 1' and 2, respectively. Here, we have done an approximate treatment. Because of the very similar luminescent properties of Complex 1' and 2, showed in Figure 1, B, we regarded approximatively the calibration cure of Complex 2 (eq. 2) as Complex 1'.

As could be seen in Figure 3, the two curves were symmetric trend but the inflection points were noticeably different. The large change rates of TEMPOH species were located at 21 min and 36 min. Nevertheless, for the concentration of TEMPO species, the turning points were located at 28 min and 43 min.

$y_{EPR} = 0.01765 + 2.02[C_1], R^2 = 0.9959(1)$)
$y_{\text{Emission}} = 0.02737 + 1.34[C_2], R^2 = 0.9962(2)$)
$C_1 = (3.8 \times 10^3 t^3 - 0.1014t^2 - 11.17t + 205.2) / (t^2 - 60.05t + 1030)(3)$)
$C_{12} = (-8.0 \times 10^{-3} t^3 + 1.283 t^2 - 67.75 t + 1197.3) / (t^2 - 75.26 t + 1532)(4)$)

At the point of 21 min, the concentration of TEMPOH species went up rapidly, which revealed the TEMPO regeneration process became slow in consuming the TEMPOH species (Scheme 3), and then the TEMPOH species were accumulated. However, the concentration of TEMPO species

changed sharply at the point of 28 min, which was tardive about 7 min compared to TEMPOH species. We speculated this might be ascribed to the delayed response of TEMPO species. For TEMPO species, because of lack of BAIB and substrates, regeneration process and oxidation process became slow, whereas the disproportionation process was not affected. It probable that regeneration process and oxidation process maintained a balance about 7 min, later on, the balance was destructed. Therefore, the concentration of TEMPO species was changed dramatically at 28 min. Similarly, the difference of the t_2 and t_4 was also 7 min.



Figure 3. Time dependence of the concentrations of Complex 1 EPR signal (red), the concentrations of Complex 1' (black) and the concentrations of subtraction (blue) TEMPO-TEMPOH) during BzOH oxidation with BAIB/Complex 1 in DMF, rt.

Consequently, with the aid of EPR and fluorescence spectrum during the oxidation reaction, the delicate balance of TEMPO and TEMPOH species was visualized. This highlighted the bifunctional role of Complex 1 and an effective catalyst in the oxidation reaction.

Conclusions

In conclusion, we designed and synthesized a bifunctional probe which exhibited EPR signal and emission signal in a reaction. In order to understand more about the quantitative concentration changes of TEMPO/TEMPOH species during the in-situ reaction, a strategy of coupled EPR/fluorescence techniques was proposed.

During the alcohol oxidation by BAIB/Complex 1 system, the two in-situ forms of TEMPO⁺ and TEMPOH species reacted with substrates and mole equivalent BAIB, respectively. By means of the simultaneous EPR-Photoluminescence spectroscopic analysis, we could easily get the information of the delicate balance between alcohol and BAIB. After the reaction, the Complex 1 was terminated in the states of TEMPOH species revealed by the emission spectrum.

As far as we know, the alkynylplatinum(II) terpyridine-TEMPO catalyst is a new kind of bifunctional probe, and this is the first

example of combined EPR-photoluminescence spectra to give an extremely direct and quantitative evidence for the mechanistic studies in the alcohol oxidation. Hence, more mechanistic information of reaction rate in each step of the reaction cycle reinforced the previous proposals, and those details of the in-situ information allow not only can quantificationally detect the composition of working catalyst, but also can modulate the catalytic components for increased activity. This method highlighted the advantage of the new combining spectroscopic methods and can be potentially applied in other catalytic reaction in which TEMPO is used as catalyst.

Experimental Section

Materials and physical measurements

We measured the emission and UV-Vis spectra by an Edinburgh instruments FLS 920 spectrophotometer and an analytic Shimadzu UV/Vis spectrophotometer. EPR spectrometer used was a computer-controlled X-band (9.5 GHz) EPR spectrometer (Bruker A300). In order to adjust the temperature, a Bruker ER 4131VT variable temperature accessory control unit was equipped. In this way, the temperature can be control in accuracy of ± 0.1 K. We set typical ESR parameters as follows: sweep width was 60 G; 9.439 GHz was the microwave frequency; receiver gain was 1.59×10^3 ; center field was 3508 G; power was 15.99 mW; the modulation frequency was 100 kHz; the amplitude was 1 G; the conversion time was 42 msec and time constant was 10.24 msec with 1 X-scans for each 6144-point spectrum. GC-2010 (SHIMADZU) equipped with an automatic injector (SHIMADZU) was used to detect the alcohol and aldehyde.

We recorded the UV-Vis spectra at 25 °C through a quartz cell, emission dynamic experiments were recorded through a quartz cell at 25°C, and EPR dynamic experiments spectra were recorded at 25 °C through quartz capillary placed for O₂ admission.

Synthesis of Terpy-TEMPO

Synthesis of 2,2,6,6–Tetramethyl-4- (2,2':6',2'' - terpyridin-4'-yloxy)-piperidi-1-oxyl (L, terpy-TEMPO). Ligand L was prepared by a reported procedure,20 Yield 4.2 g, 90%. Melting point was located 128-130°C. ESI-MS: [M+H]⁺ 404.01, 426.13. Elemental analysis calculation for C₁₂H₂₇N₄O⁻₂: C, 71.44; H, 6.74; N, 13.90. Experiment value: C, 71.20; H, 6.70; N, 13.89.

Synthesis of chlorine salt of [Pt(terpy-TEMPO)Cl] Cl·H₂O·CH₃OH

Synthesis of [Pt(terpy-TEMPO)CI](PF6)

A 100 ml round three-necked bottle was charged with [Pt(terpy-TEMPO)Cl]Cl-H₂O-CH₃OH (0.14 g, 0.20 mmol), and dried methyl alcohol (50 mL). The mixture is stirred and heated until the various cultures melt together. And then added gradually NH₄PF₆ (2 mmol, 0.34 g) methyl alcohol solution (10 ml), immediately, the clear solution in round bottom became turbid. Stirred the mixture for about 3 h latter, the suspension became dark orange and the solid was completely precipitated. We collected the product and washed with deionized water (300 ml) for 3 times, and dried in vacuo, to obtain [Pt(terpy-TEMPO)Cl](PF₆) 0.13 g, yield 84.7%.

Synthesis of [Pt(terpy-TEMPO)(C=CPh)](PF₆)

1.0 mmol [Pt(terpy-TEMPO)CI](PF₆) (0.78 g) was mixed with 0.3 mmol Cul (0.06 g) in 100 ml DMF, sealed in a 200 ml three neck flask. The mixture was protected by a bubble filled with N₂. And then injected 2.0 mmol phenylacetylene (0.2 ml), added 3.0 mmol triethylamine (0.3 ml) subsequently. After stirring the mixture in 55 °C for about 48 h in dark place, the reaction mixture turned to dark brown solution. We treated the mixture with Et₂O (500 ml) in three times to completely precipitate ochre solids. Then we collected this solid by filtration and washed with another 10 ml Et₂O. At last, this solid were dried in vacuum drying oven. The Yield was 0.67 g (96%). ESI-MS calculation for PtC₃₂H₃₂N₄O₂ is 699.2. Found: 700.3. Calculations of elemental analysis for PtC₃₂H₃₂N₄O₂PF₆ were C, 45.40; H, 3.79; N, 6.63. Experiment value: C, 44.14; H, 3.64; N, 6.42.

Synthesis of hexafluorophosphate of [Pt(terpy)Cl](PF₆)

We prepared the chlorine salt complex, [Pt(terpy)Cl]Cl-2H₂O, according to the procedures of Burstall and Lippard,^[11, 12] then dissolved the compound [Pt(terpy)Cl]Cl-2H₂O in water, added much excess of the NH₄PF₆, stirred at 25 °C and after the counterion metathesis, precipitates were formed largely. We collected the products and washed the solid two times (10 ml Et₂O), dried overnight in vacuum drying oven.

Synthesis of [Pt(terpy)(C≡CPh)](PF₆)

1.0 mmol [Pt(terpy)Cl](PF₆) (0.61 g) was mixed with 0.3 mmol Cul (0.06 g) in 40 ml DMF, sealed in a 100 ml three neck flask. Those mixtures were protected by a bubble filled with N₂. And then injected 2.0 mmol phenylacetylene (0.2 ml), added 3.0 mmol triethylamine (0.3 ml) subsequently. After stirring the mixture in 55 °C for about 48 h in dark place, the reaction mixture turned to dark brown solution. We treated the mixture with Et₂O (500 ml) in three times to completely precipitate ochre solids. Then we collected this solid by filtration and washed with another 10 ml Et₂O. At last, this solid were dried in vacuum drying oven. The Yield was 0.60 g (82%). ESI-MS calculation for PtC₂₃H₁₆N₃: 529.1 Found: 529.2. Elemental analysis calculations of PtC₂₃H₁₆N₃PF₆: C, 40.96; H, 2.39; N, 6.23. Experiment value: C, 41.04; H, 2.37; N, 5.96.

Measurements of spectroscopic properties

We measured the UV-Vis spectra of complexes by a Jena S600 UV-Vis spectrophotometer, in room temperature (25 °C), and samples were dissolved in DMF solution, 1×10^{-4} mol. L⁻¹. Photoluminescence (PL) spectra were recorded using the spectrophotometer (FLS 920). The concentrations of samples were 1×10^{-4} mol. L⁻¹, except in the timedependence of in-situ oxidation reactions. The electrons paramagnetic resonance (EPR) signals of the TEMPO derive were recorded by using a spectrometer (Bruker A300). The concentrations of samples were also 1×10^{-4} mol. L⁻¹, except in the time-dependence of *in-situ* oxidation reactions.

Typical process for oxidation of phenylcarbinol

We chose homogeneous oxidation of benzyl alcohol as oxidation model, and apply [Pt(terpy-TEMPO)(C≡CPh)](PF₆) in the mechanism study. In a general procedure, we added 2.2 mmol BAIB (0.71 g) to 2 mmol benzyl alcohol (0.22 g) and [Pt(terpy-TEMPO)(C≡CPh)](PF₆) (0.085 g, 0.2 mmol) in the scale of 2 ml DMF, at 25 °C, temperature control accuracy at \pm 1 °C; stirring rate: 1000 r/min; oxygen pressure: 1 atm. About 1 h latter, the reaction was completed, and then the gas chromatography was used to analysis the composition of the mixture.

GC analyzed methods: The assay of residual benzyl alcohol and product were calculated according to the internal standard method, and the ortho-nitrotoluene was added as the internal standard in the test.

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Keywords: Platinum(II) terpyridine complex • TEMPO derivatives • Alcohol oxidation • EPR Spectroscopy • Fluorescence Spectroscopy

a) I. W. C. E. Arends, Y. X. Li, R. Ausan, R. A. Sheldon, *Tetrahedron* **2006**, *62*, 6659-6665; b) P. Gamez, I. W. C. E. Arends, R. A. Sheldon, J. Reedijk, *Adv. Synth. Catal.* **2004**, *346*, 805-811; c) R. A. Sheldon, I. W. C. E. Arends, *Adv. Synth. Catal.* **2004**, *346*, 1051-1071; d) K. X. Chen, P. F. Zhang, Y. Wang, H. R. Li, *Green Chem.* **2014**, *16*, 2344-2374; e) A. E. Fernandes, O. Riant, K. F. Jensen, A. M. Jonas, *Angew. Chem. Int. Ed.* **2016**, *55*, 11044-11048; f) M. Hirota, K. Furihata, T. Saito, T. Kawada, A. Isogai, *Angew. Chem. Int. Ed.* **2010**, *49*, 7670-7672; g) L. Jia, K. X. Chen, C. M. Wang, J. Yao, Z. R. Chen, H. R. Li, *RSC Adv.* **2014**, *4*, 15590-15596; h) L. Jia, K. X. Chen, L. Y. Wang, R. F. Du, C. M. Wang, J. Yao, H. R. Li, *Catal. Commun.* **2015**, *67*, 31-34.

[2] a) W. F. Bailey, J. M. Bobbitt and K. B. Wiberg, *J. Org. Chem.* 2007, 72, 4504-4509; b)
A. Dijksman, A. Marino-Gonzalez, A. M. I. Payeras, I. W. C. E. Arends and R. A. Sheldon, *J. Am. Chem. Soc.* 2001, *123*, 6826-6833; c)
B. Karimi, A. Biglari, J. H. Clark and V. Budarin, *Angew. Chem. Int. Ed.* 2007, *46*, 7210-7213; d) M.F.Semmelhack, C. R. Schmid, D. A. Cortes and C. S. Chou, *J. Am. Chem. Soc.* 1984, *106*, 3374-3376; e) A. Díaz-Rodríguez, L. Martínez-Montero, I. Lavandera, V. Gotor, V. Gotor-Fernández, *Adv. Synth. Catal.* 2014, *356*, 2321–2329.
[3] a) B. Karimi, A. Biglari, J. H. Clark, V. Budarin, *Angew. Chem. Int. Ed.*

[] a) B. Karimi, A. Biglari, J. H. Clark, V. Budarin, Angew. Chem. Int. Ed. 2007, 46, 7210-7213; b) R. H. Liu, X. M. Liang, C. Y. Dong, X. Q. Hu, J.

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Am. Chem. Soc. 2004, 126, 4112-4113; c) Z. Zheng, J. L. Wang, M. Zhang, L. X. Xu, J. B. Ji, ChemCatChem 2013, 5, 307–312; d) X. L. Wang, R. H. Liu, Y. Jin, X. M. Liang, Chem-Eur. J. 2008, 14, 2679-2685.

- [4] a) J. M. Hoover, B. L. Ryland, S. S. Stahl, J. Am. Chem. Soc. 2013, 135, 2357-2367; b) J. M. Hoover, S. S. Stahl, J. Am. Chem. Soc. 2011, 133, 16901-16910; c) J. E. Steves, S. S. Stahl, J. Org. Chem. 2015, 80, 11184-11188; d) A. Dijksman, A. Marino-Gonzalez, A. M. I. Payeras, I. W. C. E. Arends, R. A. Sheldon, J. Am. Chem. Soc. 2001, 123, 6826-6833; e) P. Gamez, I. W. C. E. Arends, J. Reedijk, R. A. Sheldon, Chem. Commun. 2003, 2414-2415; f) P. Gamez, I. W. C. E. Arends, R. A. Sheldon, J. Reedijk, Adv. Synth. Catal. 2004, 346, 805-811; g) R. A. Sheldon, I. W. C. E. Arends, J. Mol. Catal. A-chem. 2006, 251, 200-214; h) S. A. Tromp, I. Matijosyte, R. A. Sheldon, I. W. C. E. Arends, G. Mul, M. T. Kreutzer, J. A. Moulijn, S. de Vries, ChemCatchem, 2010, 2, 827-833.
- a) M. A. Banares and G. Mestl, Adv. Catal. 2009, 52, 43-128; b) A.
 Bruckner, Adv. Catal. 2007, 51, 265-308; c) A. T. Yordanov, K. Yamada,
 M. C. Krishna, J. B. Mitchell, E. Woller, M. Cloninger, M. W. Brechbiel,
 Angew. Chem. Int. Ed. 2001, 40, 2690-2692.
- [6] a) Robert A. Schoonheydt, *Chem. Soc. Rev.* 2010, 39, 5051–5066; b) Alexandre Vimont, Frederic Thibault-Starzyk and Marco Daturi, *Chem. Soc. Rev.* 2010, 39, 4928–4950; c) T. A. Nijhuis, S. J. Tinnemans, T. Visser and B. M. Weckhuysen, *Phys. Chem. Chem. Phys.* 2003, 5, 4361-4365.
- [7] J. Rabeah, U. Bentrup, R. Stosser, A. Bruckner, Angew. Chem. Int. Ed. 2015, 54, 11791-11794.
- [8] a) P. Chen, W. L. Xu, X. C. Zhou, D. Panda, A. Kalininskiy, *Chem. Phys. Lett.* 2009, *470*, 151-157; b) W. L. Xu, J. S. Kong, P. Chen, *J. Phys. Chem. C* 2009, *113*, 2393-2404; c) W. L. Xu, J. S. Kong, P. Chen, *Phys. Chem. Chem. Phys.* 2009, *11*, 2767-2778; d) W. L. Xu, J. S. Kong, Y. T. E. Yeh, P. Chen, *Nat. Mater.* 2008, *7*, 992-996; e) W. L. Xu, H. Shen, Y. J. Kim, X. C. Zhou, G. K. Liu, J. Park, P. Chen, *Nano. Lett.* 2009, *9*, 3968-3973; f) W. L. Xu, H. Shen, G. K. Liu, P. Chen, *Nano. Research* 2009, *2*, 911-922; g) X. C. Zhou, W. L. Xu, G. K. Liu, D. Panda, P. Chen, *J. Am. Chem. Soc.* 2010, *132*, 138-146; h) H. Shen, W. L. Xu, P. Chen, *Phys. Chem. Chem. Phys.* 2010, *12*, 6555-6563.
- a) M. Chiesa, E. Giamello, M. Che, *Chem. Rev.* 2010, *110*, 1320-1347;
 b) K. Dyrek, M. Che, *Chem. Rev.* 1997, *97*, 305-331; c); d) Z. Sojka, *Catal. Rev.* 1995, *37*, 461-512.

- [10] a) M. A. Banares, I. E. Wachs, J. Raman. Spectrosc. 2002, 33, 359-380; b) B. M. Weckhuysen, Chem. Commun. 2002, 97-110; c) M. G. O'Brien, A. M. Beale, S. D. M. Jacques, M. Di Michiel and B. M. Weckhuysen, ChemCatChem, 2009, 1, 99–102; d) T. Burgi, J. Catal. 2005, 229, 55–63; e) M. Caravati, J.-D. Grunwaldt and A. Baiker, Phys. Chem. Chem. Phys. 2005, 7, 278–285; f) L. R. Knopke, N. Nemati, A. Kockritz, A. Bruckner and U. Bentrup, ChemCatChem, 2010, 3, 273–280.
- [11] G. T. Morgan; F.H. Burstall. J. Chem. Soc. 1934, 1498-1500.
- [12] K. W. Jennette, J. T. Gill, J. A. Sadownick and S. J. Lippard, J. Am. Chem. Soc. 1976, 98, 6159-6168.
- [13] L. Yin, C. Liang, K. X. Chen, C. X. Zhao, J. Yao, H. R. Li, Acta. Phys. -Chim. Sin. 2017, 33, 1390-1398.
- [14] a) K. M. C. Wong, W. H. Lam, Z. Y. Zhou, V. W. W. Yam, Chem. *Eur. J.* 2008, *14*, 10928-10931; b) V. W. W. Yam, K. M. C. Wong, N. Y. Zhu, *Angew. Chem. Int. Ed.* 2003, *42*, 1400-1403; c) V. W. W. Yam, K. H. Y. Chan, K. M. C. Wong, B. W. K. Chu, *Angew. Chem. Int. Ed.* 2006, *45*, 6169-6173; d) C. Yu, K. M. C. Wong, K. H. Y. Chan, V. W. W. Yam, *Angew. Chem. Int. Ed.* 2005, *44*, 791-794.
- [15] A. DeMico, R. Margarita, L. Parlanti, A. Vescovi and G. Piancatelli, J. Org. Chem. 1997, 62, 6974-6977.
- [16] V. A. Golubev, E. G. Rozantsev, M. B. Neiman. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 1927-1936; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1965**, 1898-1904.
- [17] J. M. Bobbitt, M. C. L. Flores, *Heterocycles* **1988**, *27*, 509-533; b) W. Brackman, C. J. Gaasbeek, Recl. *Trav. Chim. Pays-Bas*, **1966**, *85*, 221-241.
- [18] A. E. J. deNooy, A. C. Besemer and H. vanBekkum, Synthesis-stuttgart, 1996, 1153-1174.
- a) W. X. Qian, E. L. Jin, W. L. Bao, Y. M. Zhang, *Angew. Chem. Int. Ed.* **2005**, *44*, 952-955; b) A. M. P. Salvo, V. Campisciano, H. A. Beejapur,
 F. Giacalone, M. Gruttadauria, *Synlett*, **2015**, *26*, 1179-1184.
- [20] M. A. Halcrow; E. K. Brechin; E. J. L McInnes. J. Chem. Soc. Dalton Trans. 1998, 15, 2477-2482.

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Entry for the Table of Contents

FULL PAPER

A TEMPO-mediated platinum terpyridine complex was designed and synthesized. This complex showed switchable signals of EPR and photoluminescence in situ states, which can serve as catalyst and bifunctional probe during the reaction. Hereby, a method combined EPR and fluorescence spectra was established and applied successfully to study the mechanism of alcohol oxidation.



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