

Copper(II) Complexes Based on 4'-R-Terpyridine: Synthesis, Structures, and Photocatalytic Properties

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Abstract Complexes Cu(II)(4'-R-terpyridine)₂(ClO₄)₂[R=2-thienyl(1), 2-(5-bromothieryl)(2), 2-(5-methylthienyl)(3) and 2-(5-methoxythienyl)(4)] were synthesized, and their structures were determined by single-crystal X-ray diffraction analyses and were further characterized by high resolution mass spectrometry, infrared spectroscopy (IR), as well as elemental analysis. Single crystal X-ray diffraction analysis shows that Cu(II) ions in the complexes are both six-coordinated with N₆ coordination sphere, displaying distorted octahedral geometries. In addition, the UV-Vis absorption spectra show that the four complexes all exhibit absorption components in both UV and visible light regions. Thus, the photocatalytic activities of the four complexes in the degradation of organic dyes were investigated.

Keywords Copper(II) complex; Single crystal structure; Photocatalytic property

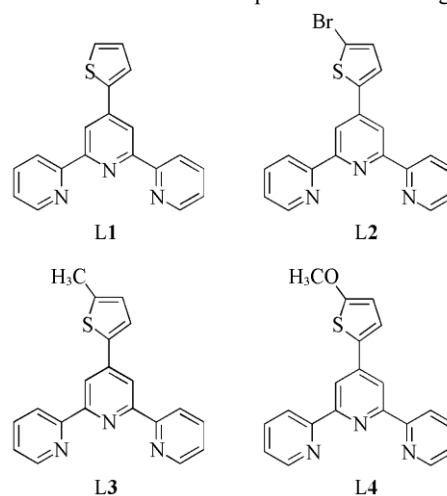
1 Introduction

Owing to their stability combined with fascinating electrochemical, photophysical and photochemical properties, the coordination chemistry of 2,2':6',2''-terpyridines (tpy) has been one of the most interesting research topics in the past decades^[1–4]. Most of the tpy complexes are in either [M(tpy)]ⁿ⁺ or [M(tpy)₂]ⁿ⁺ form, with one or two tpy ligands coordinated to the metal centers. Compared with 2,2'-bipyridine (bpy), one of the negative aspects of tpy is that the photophysical properties of [M(tpy)₂]ⁿ⁺ are frequently inferior to those of [M(bpy)₃]ⁿ⁺^[5]. Thus, the expansion of the photoreponse region and the enhancement of the quantum yield of [M(tpy)₂]ⁿ⁺ and [M(tpy)]ⁿ⁺ become urgent problems in the investigation of tpy based photocatalysts. It has been proved that attaching π -conjugated groups to tpy would improve the photophysical properties, as well as allow electronic communication between tpy and the appended functionality^[6–12]. The introduction of a 2-thienyl group to the 4'-position should result in remarkable broadening of the tpy absorption band and an overall increase in its intensity^[13–18].

So far, [Cu(tpy)₂]²⁺ has been well-investigated^[19–28]. However, very few studies concerning the coordination of Cu(II) to one or two tpy ligands bearing conjugated thienyl groups at 4'-position have been reported^[29–35]. Recently, Rahiman *et al.*^[36] reported a series of bis(terpyridine)copper(II) complexes with π -conjugated groups at 4'-position, which might act as DNA-targeted metallo-anticancer agents to overcome cisplatin resistance.

In this study, tpy was used as a basic skeleton, on which 2-thienyl, 2-(5-bromothieryl), 2-(5-methylthienyl) and 2-(5-methoxythienyl) groups were attached at the

4'-position (Scheme 1). Complexes 1–4 were synthesized, and their structures were determined by single-crystal X-ray diffraction analysis and were further characterized by high resolution mass spectrometry, infrared spectroscopy (IR), as well as elemental analysis. In addition, the optical band gaps, and photocatalytic behaviors of these complexes were investigated.



Scheme 1 Structures of the ligands used in this work

2 Experimental

2.1 Materials and Methods

All starting materials were purchased from commercial suppliers and used without further purification. Solvents were used as received. ¹H and ¹³C NMR spectra were recorded on a Bruker AV400 spectrometer. Chemical shifts are reported in δ relative to tetramethylsilane (TMS) as standard. High resolution mass spectra (HRMS) were collected on a Bruker Apex IV

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FTMS using ESI(electrospray ionization). IR spectra were obtained on a Nicolet Magna-IR 750 spectrometer. The solid-state UV-Vis spectra for powder samples were recorded on a Perkin-Elmer Lambda 35 UV-Vis spectrometer equipped with an integrating sphere using BaSO₄ as the white standard. Single crystal X-ray diffraction measurements for complexes **1** and **4** were carried out on a computer-controlled Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromatized Mo K α with a radiation wavelength of 0.071073 nm using ω -scan mode. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXS 97^[37] and SHELXL 97 programs^[38]. Semiempirical absorption corrections were applied using SADABS program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent or constrained refinement. Photocatalytic experiments: the UV light source was a 375 W high-pressure mercury lamp(main output of 365 nm), while the visible light source was a 500 W halogen lamp with a UV cut-off filter(providing visible light with $\lambda > 420$ nm). A suspension of powdered catalyst(30 mg) in fresh aqueous solution of RhB(100 mL, 1×10^{-5} mol/L) was first sonicated for 5 min, and then shaken at a constant rate in the dark to establish an adsorption/desorption equilibrium of RhB on the sample surface. At given irradiating intervals, a series of suspension of a certain volume was collected and filtered through a membrane filter(pore size, 0.45 μ m) to remove the suspended catalyst particles. The organic dye concentration was estimated by the absorbance at 554 nm, which directly related to the structural change of its chromophore.

2.2 Synthesis

The synthetic methodology for **L1** and **L2** has been previously described^[12]. **L3** and **L4** were synthesized following that methodology(see the Electronic Supplementary Material of this paper). Complexes **1**—**4** were obtained by reacting copper(II) perchlorate with the appropriate ligand in dimethylformamide(DMF).

Synthesis of ligand L3: 5-methylthiophene-2-carbaldehyde(1.70 g, 13.5 mmol) was added to a mixture of 2-acetylpyridine(3.27 g, 27.0 mmol) and NH₄OH(52 mL, 25% aqueous solution) in ethanol(200 mL). Subsequently, KOH(1.91 g, 34.0 mmol) was slowly added to the mixture, and the resulting mixture was stirred at room temperature overnight, the precipitate was then collected and recrystallized from CHCl₃-CH₃OH. **L3** was obtained as a white solid(2.0 g, 6.0 mmol, 44%). ¹H NMR(400 MHz, CDCl₃), δ : 8.73(d, $J=4$ Hz, 2H), 8.64(s, 1H), 8.62(s, 3H), 7.86(t, $J=8$ Hz, 2H), 7.59(d, $J=3.6$ Hz, 1H), 7.34(m, 2H), 6.82(m, 1H), 2.60(s, 3H). ¹³C NMR(100 MHz, CDCl₃), δ : 155.3(1C), 155.0(1C), 148.4(2C), 143.0(1C), 141.5(1C), 138.7(1C), 136.3(3C), 125.4(2C), 123.4(2C), 120.9(2C), 116.3(2C), 16.1(1C). HRMS, m/z , calcd. for C₂₀H₁₆N₃S[M+H]⁺: 330.106; found: 330.105. Elemental anal.(%) calcd. for C₂₀H₁₅N₃S: C 72.92, H 4.59, N 12.76; found: C 72.83, H 4.62, N 12.80. FTIR, $\tilde{\nu}/\text{cm}^{-1}$: 3033, 1579, 1398, 1162, 790.

Synthesis of ligand L4: 5-methoxythiophene-2-carbaldehyde(1.80 g, 12.6 mmol) was added to a mixture of 2-acetylpyridine(3.1 g, 25.2 mmol) and NH₄OH(50 mL, 25% aqueous solution) in ethanol(180 mL). Subsequently, KOH(1.8 g, 32.2 mmol) was slowly added to the mixture, and the resulting mixture was stirred at room temperature overnight, the precipitate was then collected and recrystallized from CHCl₃-CH₃OH. **L4** was obtained as a white solid(1.9 g, 5.5 mmol, yield 43%). ¹H NMR(400 MHz, CDCl₃), δ : 8.73(d, $J=4$ Hz, 2H), 8.62(d, $J=8$ Hz, 2H), 8.54(s, 2H), 7.87(t, $J=8$ Hz, 2H), 7.49(d, $J=3.6$ Hz, 1H), 7.35(m, 2H), 6.28(d, $J=4$ Hz, 1H), 3.97(s, 3H). ¹³C NMR(100 MHz, CDCl₃), δ : 155.3(1C), 155.0(1C), 148.3(2C), 143.1(1C), 136.2(3C), 126.8(1C), 123.8(2C), 123.3(3C), 120.8(2C), 115.4(2C), 60.3(1C). HRMS, m/z calcd. for C₂₀H₁₆N₃OS[M+H]⁺: 346.101; found: 346.099. Elemental anal.(%) calcd. for C₂₀H₁₅N₃OS: C 69.54, H 4.38, N 12.17; found: C 69.67, H 4.45, N 12.14. FTIR, $\tilde{\nu}/\text{cm}^{-1}$: 3043, 1583, 1496, 1398, 1060, 786.

Synthesis of Cu(L1)₂(ClO₄)₂(1): **L1**(136.4 mg, 0.43 mmol) was dissolved in DMF(20 mL), and Cu(ClO₄)₂·6H₂O(80.0 mg, 0.22 mmol) in DMF(5 mL) was slowly added to the solution. After the mixture was heated at 80 °C for 2 h, the solvent was removed under vacuo. The residual was washed with methanol and dried, and complex **1** was obtained as a blue solid(169 mg, 0.19 mmol, yield 87%). HRMS, m/z calcd. for C₃₈H₂₆ClN₆O₄S₄Cu[M-ClO₄]⁺: 792.044; found: 792.041. Elemental anal.(%) calcd. for C₃₈H₂₆Cl₂N₆O₈S₂Cu: C 50.10, H 2.93, N 9.41; found: C 50.43, H 3.23, N 9.05. FTIR, $\tilde{\nu}/\text{cm}^{-1}$: 3077, 1612, 1427, 1089, 790.

Synthesis of Cu(L2)₂(ClO₄)₂(2): **L2**(170.0 mg, 0.43 mmol) was dissolved in DMF(20 mL), and Cu(ClO₄)₂·6H₂O(80.0 mg, 0.22 mmol) in DMF(5 mL) was slowly added to the solution. After the mixture was heated at 80 °C for 2 h, the solvent was removed under vacuo. The residual was washed with methanol and dried, and complex **2** was obtained as a blue solid(178 mg, 0.17 mmol, yield 77%). HRMS, m/z calcd. for C₃₈H₂₄Br₂ClN₆O₄S₂Cu[M-ClO₄]⁺: 947.865; found: 947.863. Elemental anal.(%) calcd. for C₃₈H₂₄Br₂Cl₂N₆O₈S₂Cu: C 43.43, H 2.30, N 8.00; found: C 43.89, H 2.63, N 7.89. FTIR, $\tilde{\nu}/\text{cm}^{-1}$: 3091, 1610, 1427, 1085, 790.

Synthesis of Cu(L3)₂(ClO₄)₂(3): **L3**(142.1 mg, 0.43 mmol) was dissolved in DMF(20 mL), and Cu(ClO₄)₂·6H₂O(80.0 mg, 0.22 mmol) in DMF(5 mL) was slowly added to the solution. After the mixture was heated at 80 °C for 2 h, the solvent was removed under vacuo. The residual was washed with methanol and dried, complex **3** was obtained as a blue solid(172 mg, 0.19 mmol, yield 82%). HRMS, m/z calcd. for C₄₀H₃₀ClN₆O₄S₂Cu[M-ClO₄]⁺: 820.075; found: 820.072. Elemental anal.(%) calcd. for C₄₀H₃₀Cl₂N₆O₈S₂Cu: C 52.15, H 3.28, N 9.12; found: C 53.56, H 3.60, N 9.03. FTIR, $\tilde{\nu}/\text{cm}^{-1}$: 3074, 1608, 1423, 1079, 860.

Synthesis of Cu(L4)₂(ClO₄)₂(4): **L4**(149.6 mg, 0.43 mmol) was dissolved in DMF(20 mL), and Cu(ClO₄)₂·6H₂O(80.0 mg, 0.22 mmol) in DMF(5 mL) was slowly added to the solution. After the mixture was heated at 80 °C for 2 h, the solvent was removed under vacuo. The residual was washed with methanol and dried, and complex **4** was obtained as a blue solid(159 mg,

0.17 mmol, yield 76%). HRMS, m/z , calcd. for $C_{40}H_{30}ClN_6O_6S_2Cu[M-ClO_4]^+$: 852.065; found: 852.060. Elemental anal.(%) calcd. for $C_{40}H_{30}Cl_2N_6O_{10}S_2Cu$: C 50.40, H 3.17, N 8.82; found: C 50.79, H 3.40, N 8.63. FTIR, $\tilde{\nu}/\text{cm}^{-1}$: 3069, 1609, 1479, 1423, 1083, 860.

3 Results and Discussion

3.1 Description of Crystal Structures

Crystals of complexes **1** and **4** suitable for structure determinations were obtained by vapor diffusion of methanol into the DMF solution of the corresponding complex. X-Ray diffraction measurements were carried out at 113 K. Despite their crystallization from the same medium, complexes **1** and **4**

do not have identical space group. Basic crystallographic data are summarized in Table 1.

$Cu(L1)_2(ClO_4)_2(CH_3OH)_{1.25}$: single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in a triclinic crystal system and $P\bar{1}$ space group. The asymmetric unit consists of two crystallographically independent Cu(II) ions, which are both six-coordinated to N6 coordination sphere derived from two different chelating ligands. However, the bond lengths and angles for the two Cu(II) ions are slightly different. The Cu1—N and Cu2—N lengths are in the ranges of 0.1948(12)—0.2344(15) nm and 0.1941(13)—0.2292(16) nm, respectively. Thus, the coordination geometries of them both display distorted octahedron geometries. In complex **1**(Fig.1), the three pyridine rings of each L1 ligand are in a *cis-cis*

Table 1 Crystallographic data for complexes 1 and 4

Complex	1	4
Chemical formula	$C_{39.25}H_{31}Cl_2CuN_6O_{9.25}S_2$	$C_{41.25}H_{35}Cl_2CuN_6O_{11.25}S_2$
Formula weight	933.26	993.31
Temperature/K	113(2)	113(2)
Wavelength/nm	0.071073	0.071073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/nm	1.5662(3)	4.1761(8)
b/nm	1.6118(3)	0.91702(18)
c/nm	1.7251(4)	2.4923(5)
$\alpha/^\circ$	98.19(3)	90
$\beta/^\circ$	96.59(3)	118.05(3)
$\gamma/^\circ$	113.41(3)	90
Volume/ nm^3	3.8846(13)	8.423(3)
Z, calculated density/(Mg m^{-3})	4, 1.596	8, 1.567
Absorption coefficient/ mm^{-1}	0.874	0.815
θ range for data collection/ $^\circ$	1.41—25.02	1.85—25.02
Limiting index	$-18 \leq h \leq 18, -19 \leq k \leq 19, -19 \leq l \leq 20$	$-49 \leq h \leq 49, -9 \leq k \leq 10, -27 \leq l \leq 29$
$F(000)$	1910	4076
Reflection collected/unique	32686/13652 [$R(\text{int})=0.0401$]	30104/7379 [$R(\text{int})=0.0573$]
Goodness-of-fit on F^2	1.036	1.053
Final R index [$I > 2\sigma(I)$]	$R_1=0.0611, wR_2=0.1571$	$R_1=0.0987, wR_2=0.2134$
R index (all data)	$R_1=0.0775, wR_2=0.1705$	$R_1=0.1085, wR_2=0.2191$
Largest diff. peak and hole/($e \text{ nm}^{-3}$)	1286 and -1150	1135 and -609

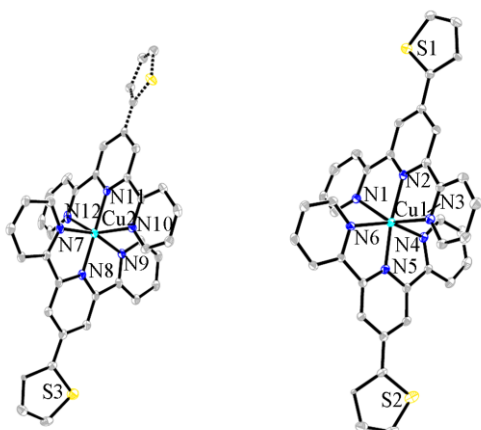


Fig.1 Coordination environment of Cu(II) ions in complex 1 with 30% probability thermal ellipsoids

Anions, solvent molecules and hydrogen atoms are omitted for clarity. conformation and coordinates Cu(II) ion with their tridentate sites to form mononuclear unit. In addition, for each crystallographically independent Cu(II) ion, the dihedral angles between

the two L1 ligands are 89.3° (Cu1) and 95.2° (Cu2), respectively. Furthermore, these mononuclear units are assembled into a 3D network by hydrogen bonds and π - π stacking interactions(Fig.2).

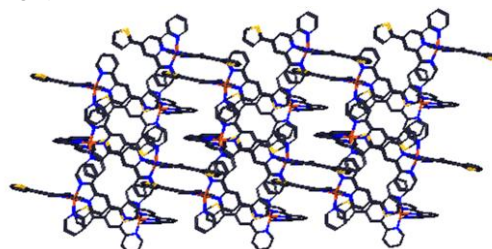


Fig.2 3D network of complex 1

$Cu(L4)_2(ClO_4)_2(CH_3OH)_{1.25}$: single crystal X-ray diffraction analysis reveals that complex **4** is a monomeric entity. In contrast with complex **1**, it crystallizes in a monoclinic crystal system and $C2/c$ space group. The asymmetric unit consists of one crystallographically independent Cu(II) ion, two L4 ligands, two perchlorate ions and 1.25 methanol molecules(Fig.3). Similar to complex **1**, the Cu(II) ion is also six-coordinated to

six nitrogen atoms from two L4 ligands. The Cu—N lengths are in the range of 0.1937(5)—0.2317(6) nm. Thus, the Cu(II) ion also displays a distorted octahedral geometry. In complex 4, each L4 ligand also adopts a tridentate chelating mode to link Cu(II) ion into mononuclear unit. The dihedral angles between the central pyridine ring and the adjacent pyridine rings are 11.3° and 13.3°, respectively. The dihedral angle between the two L4 ligands is 96.3°. Furthermore, these mononuclear units are assembled into a 3D network by hydrogen bonds and π - π stacking interactions(Fig.4).

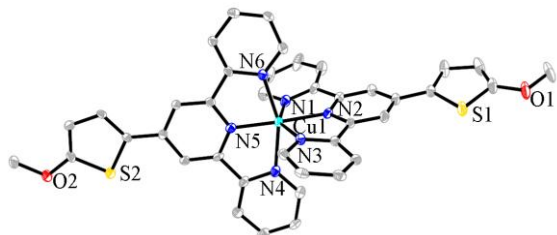


Fig.3 Coordination environment of Cu(II) ion in complex 4 with 30% probability thermal ellipsoids

Anions, solvent molecules and hydrogen atoms are omitted for clarity.

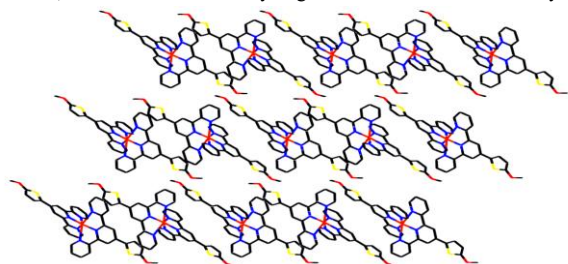


Fig.4 3D network of complex 4

3.2 Photocatalytic Activities

To elucidate the photoresponse wavelength region, the diffuse reflectivity UV-Vis spectra for ligands and complexes were recorded in the crystalline state at room temperature (Fig.5). The free ligands exhibit strong absorption bands in the

UV region, which can be ascribed to $\pi^* \rightarrow \pi$ transitions. Complexes 1—4 show two absorption bands in both UV and visible light regions. The low energy band at 690—710 nm for these complexes can be considered as metal-to-ligand charge-transfer(MLCT) transitions, whereas the energy bands from 295 nm to 315 nm for complex 1, from 290 nm to 310 nm for complex 2, from 300 nm to 320 nm for complex 3, and from 315 nm to 335 nm for complex 4 can be assigned as $d-d$ transitions. The precise values of the band gap(E_g), obtained from Tauc equation are shown in Fig.5. The E_g values assessed from the steep absorption edge for complexes 1—4 are 2.75, 2.70, 2.65 and 2.45 eV, respectively(Fig.6).

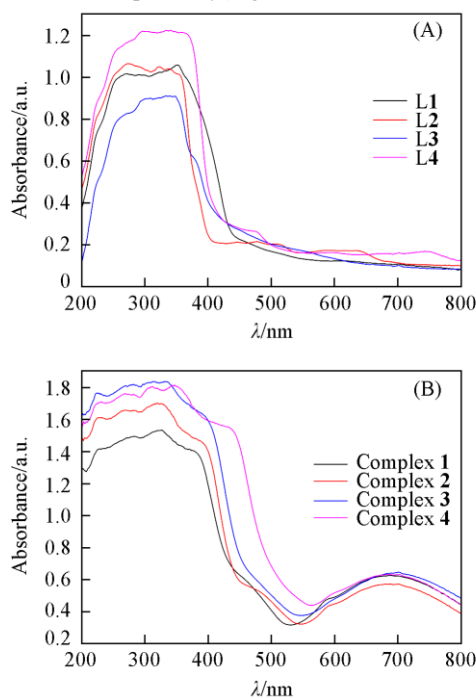


Fig.5 Diffuse reflectivity UV-Vis spectra of ligands(A) and complexes(B) with BaSO₄ as the background

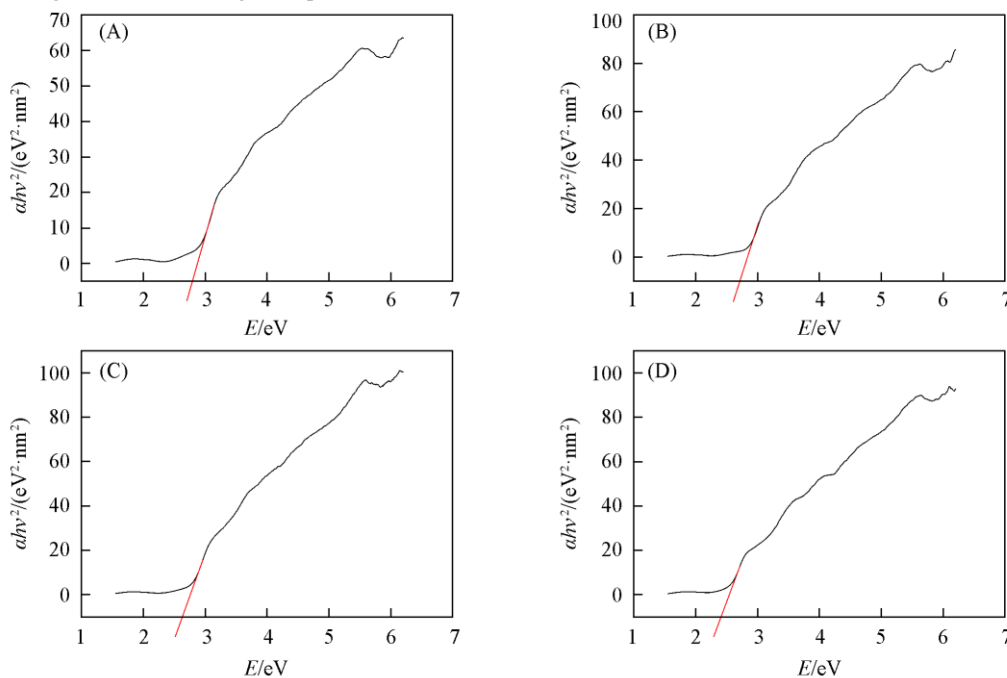


Fig.6 Tauc plots for complexes 1—4(A—D)

The presence of visible regions transitions motivated us to explore the applications of complexes **1**–**4** in heterogeneous photocatalysis. Herein, RhB, as a model of dye contaminant, was selected for evaluating the activities of photocatalysts in the purification of wastewater. We investigated the photocatalytic performances of complexes **1**–**4** in the photodegradation of RhB under light illumination. Before the photocatalytic assays were started, the samples were stirred in the dark in order to reach the adsorption-desorption equilibrium. In addition, control experiments on the photodegradation of RhB were also

carried out. While no degradation was observed with catalyst only in the absence of light illumination, the concentration of RhB almost did not change for every measurement in the presence of complexes **1**–**4**. Illumination in the absence of complexes **1**–**4** also did not result in the photocatalytic decolorization of RhB. Therefore, the presence of both illumination and complexes **1**–**4** is necessary for the efficient degradation of RhB. The concentrations of RhB(*c*) versus reaction time(*t*) of complexes **1**–**4** are plotted in Fig.7.

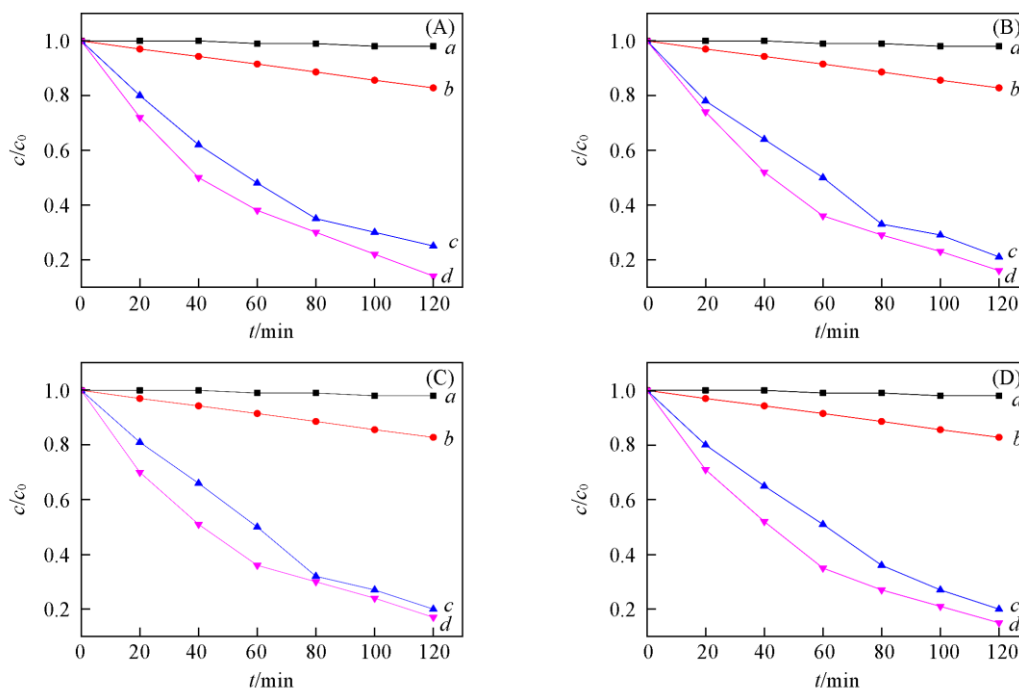


Fig.7 Concentration changes of RhB as a function of irradiation time for complexes 1–4(A–D), respectively

Conditions: *a*. visible light, without catalyst; *b*. UV light, without catalyst; *c*. visible light, with catalyst; *d*. UV light, with catalyst.

The shorter degradation time compared with the control experiments indicates that complexes **1**–**4** are active for the degradation of RhB in the presence of visible light or UV light. In addition, the photostabilities of complexes **1**–**4** were monitored by infrared spectroscopy and XRD during the course of photocatalytic reactions. The infrared spectra and XRD patterns were nearly identical to those of the original complexes, which indicates that complexes **1**–**4** remain unchanged after the photocatalytic reactions, implying that they can be used as stable catalysts for the photodegradation of RhB (see the Electronic Supplementary Material of this paper).

4 Conclusions

We synthesized and characterized the complexes Cu(II)-(4'-R-terpyridine)₂(ClO₄)₂[R=2-thienyl(**1**), 2-(5-bromothieryl) (**2**), 2-(5-methylthienyl)(**3**) and 2-(5-methoxythienyl) (**4**)]. The four complexes all exhibited absorption components both in the UV and visible light regions. Remarkably, the photocatalytic behaviors of complexes **1**–**4** indicate that they may be good and stable photocatalysts in the photodegradation of RhB under UV light or visible light. Comprehensive studies on the coordination of ligands **L1**, **L2**, **L3** and **L4** to other metals are

currently underway.

Acknowledgements

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Supplementary Data

CCDC 1415694 and 1415695 contain the supplementary crystallographic data for the complex **1** and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s40242-017-6319-3>.

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