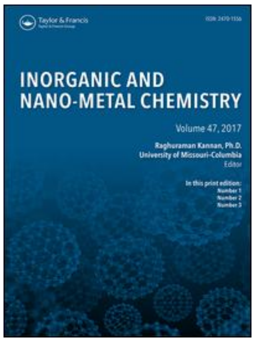

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Two New Zinc(II) and Cadmium(II) complexes of a semi-rigid bis(2-benzimidazole): Synthesis and Characterization

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Abstract

two new complexes Zn(TBimE)Cl_2 **1** and Cd(TBimE)$(I)_2$ **2** based on a semi-rigid ligand TBimE (TBimE = (E)-1,2-bis(2-benzimidazolyl)ethane) have been synthesized and their structures have been determined by X-ray single crystal diffractometry. X-ray diffraction analysis reveal that the "trans" TBimE converted to "cis" conformation in the structures of the complexes, so that the TBimE can be used as bidentate ligand to chelate the Zinc(II) and Cadmium(II) ions. Both **1** and **2** exhibit distorted tetrahedral geometries and the central metal atoms are coordinated by two N atoms from TBimE and two anions. The *UV-vis* and emission spectra show that the absorption and emission of the complexes are both assigned to the intraligand transitions and intraligand fluorescence, respectively.

Keywords

Zinc(II) complex, Cadmium(II) complex, Bis(benzimidazoles), Crystal structure

Introduction

The coordination chemistry of bis(benzimidazole) compounds have aroused much interest in recent years. For example, the compounds can be used as geometrically constraining ligands [1], and assembled into supramolecular complexes with transition metal ions [2-8]. These complexes based on bis(benzimidazole) compounds also exhibit excellent properties, such as optics [4,9-11], catalysis [4-8, 12,13], magnetism [1,14], and mimicking biological systems [15-17].

The complexes containing bis(2-benzimidazole) ligands have been studied extensively. The spacer *X* of bis(2-benzimidazole) (Chart 1) can be flexible, semi-rigid or rigid. The mononuclear [18-20], binuclear [2, 21-23] and multinuclear [3,9] complexes can be formed by changing the length of the bridging alkane chain of flexible bis(2-benzimdazolyl)alkanes ligands, the anions and the solutions. However, the studies on the complexes of bis(2-benzimidazolyl) with semi-rigid or rigid spacer are yet very poor [1, 24, 25]. Our group have investigated some complexes based on a rigid bis(2-benzimidazole) ligand[26-28], which is 1,2-bis(2-benzimidazolyl)benzene (OBimB). The OBimB ligand can form ML2 or ML mononuclear complexes with transition metal ions. In this paper, we report two new Zinc(II) and cadmium(II) complexes with a semi-rigid bis(2-benzimidazole) ligand TBimE, Zn(TBimE)$(Cl)_2$ (**1**) and Cd(TBimE)$(I)_2$ (**2**). The free ligand with "trans" configuration is changed to "cis" in its complex. The absorption and fluorescence properties of these compounds have also been studied.

Experimental

Materials and measurement

The chemical reagents which were used to synthesize TBimE and its complexes were purchased commercially and used without further purification. Elemental analyses (C, H and N) were taken on a Perkin--Elmer 1400C analyzer. IR spectra were recorded on a Nicolet 170SX spectrometer in the range of 400---4000cm^{-1} with pressed KBr pellets. UV-Vis spetra and luminescence spectra were measured on a Perkin--Elmer UV-vis spectrometer and a Hitachi F-4600 fluorescence spectrophotometer, respectively.

Synthesis of the complex

The acid-amine condensation method was used to synthesize (E)-1,2-bis(2-benzimidazolyl)ethane(TBimE) [25]. Fumaric acid (2.32g, 20mmol) and *o*-diaminobenzene (4.7g, 44mmol) were finely ground for half an hour, then heated to 200°C in 40mL polyphosphoric acid with oil bath for 3 h. The reaction solution was cooled to 100°C at the room temperature and poured into ice water with vigorous stirring. Then the yellow precipitate was formed, filtered and neutralized in a saturated sodium bicarbonate solution for 10 h. The solid was filtered off and dried, recrystallized from methanol to give yellow product (Yield, 45%). IR(KBr, cm^{-1}): 1614(w) ($\nu_{C = C, C = N}$), 1512(w), 1436(m) ($\nu_{C = C, C = N}$), 1414(m), 1350(s), 1281(w) ($\nu_{C\text{-}N}$), 1015(m), 729(s).

Zn(TBimE)(Cl)$_2$ (***1***): $ZnCl_2$•$2H_2O$ (0.020g, 0.15mmol) and TBimE (0.013g, 0.05mmol) were added to methanol (10mL) and acetonitrile (10mL), and the mixture was stirred and refluxed for half an hour. Then the light brown solution was obtained. The solution was filtered and the filtrate was left to stand at ambient environment for 2 days, and the light brown block crystals (yield: 28%) precipitated, which could be used for structural determinations. IR(KBr, cm^{-1}): 1608(w) ($\nu_{C = C, C = N}$), 1516(w), 1424(m) ($\nu_{C = C, C = N}$), 1417(m), 1350(s), 1287(w) ($\nu_{C\text{-}N}$), 1012(m), 723(s). Anal. Calcd(%) for $C_{16}H_{12}C_{l2}N_4Zn$: C, 48.45%, H, 3.05%, N, 14.13%; found(%): C, 48.48%, H, 3.07%, N, 14.16%.

*Cd(TBimE)(I)$_2$ (**2**)*: CdI_2 (0.073g, 0.15mmol) and TBimE (0.013g, 0.05mmol) were added to methanol (10mL) and acetonitrile (10mL), and the mixture was stirred and refluxed for half an hour. Then the light brown solution was obtained. The solution was filtered and the filtrate was left to stand at ambient environment for 3 days, and the light brown block crystals (yield: 28%) precipitated, which could be used for structural determinations. IR(KBr, cm^{-1}): 1605(w) ($\nu_{C = C, C = N}$), 1522(w), 1430(m) ($\nu_{C = C, C = N}$), 1412(m), 1352(s), 1283(w) ($\nu_{C\text{-}N}$), 1015(m), 719(s). Anal. Calcd(%) for $C_{24}H_{24}I_2N_6Cd$: C, 37.79%, H, 3.17%, N, 11.02%; found(%): C, 37.83%, H, 3.20%, N, 11.22%.

X-ray crystallography

A methanol and acetonitrile solution of TBimE, $HgCl_2$ was left to stand at room temperature and afforded the crystals of TBimE. Crystallographic data of the TBimE and its complexes were recorded at 293(2) K on a Bruker SMART 1000 CCD area detector X-ray single crystal diffractometer with graphite-monochromated Mo Kα radiation (λ＝0.071073 nm) and a ω-scan mode. The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least squares with SHELXL [29, 30]. Metal atom in the complex was located from E-map. The non-hydrogen atoms were positioned by subsequent least-squares refinement and difference fourier calculations. All the non-hydrogen atoms were refined anisotropically. The solvent molecules in **2** can not be solved for their disorders. The H atoms were generated theoretically onto their parent atoms and refined isotropically with fixed thermal factors. A summary of crystal data and structure refinements for TBimE and the complexes are provided in Table 1. Selected bond lengths and angles are listed in Table 2.

Results and discussion

Crystal structure of the complexes

As shown in Fig.1a, the TBimE molecule exhibits “trans” configuration and the benzimidazole rings locate at the opposite direction. The dihedral angle between two benzimidazole rings is 28.84°. The central Zn atom in **1** is coordinated by two N atoms from a TBimE ligand and two Cl^{-} anions to form a tetrahedral geometry(Fig.1b). The TBimE as a bidentate ligand chelates a Zinc(II) ion to form seven-member ring structure. The bond angles around Zn atom are from 104.6(2)° to 111.1(2)°, which are deviated from 109°28', to result in a distortable tetrahedron. The Zn-N distances are almost equal (Zn-N(1) = 0.2001(5) and Zn-N(3) = 0.2008(6) nm, which is close to the bond lengths of $Zn\text{-}N_{benzimidazole}$[27]). The Zn-Cl bond lengths are 0.2242(2) and 0.2252(2) nm, respectively. Interestingly, the “trans” structure of the free TBimE converted to the “cis” in the complex, as a result of the coordination role with the metal ion. The two rings of TBimE ligand are almost coplanar with a dihedral angle of 9.20°, and the Zinc atom is almost in the plane. Complex unit is hydrogen bonded to the other between the amine NH group of TBimE ligand and the Cl atom(N2-$Cl2^{i}$, 0.3206(6)nm; symmetry codes: ^{i} 2-*x*, 1-*y*, 1-*z*). The N•••Cl distances are in the range of N-H•••Cl hydrogen bonding (0.291-0.362nm). [31] There are also the π-π interactions with a face to face distance of 0.3534(4) nm between the imidazole rings of two adjacent complex unit. These hydrogen bonds and π-π interactions link complex units into a one-dimensional (1-D) chain (Fig. 2).

Complex **2** is structurally analogous to complex **1**(Fig. 3). The Cd^{II} center has a tetrahedral coordination geometry, which is formed by two nitrogen donor atoms of TBimE and two I^{-} anion. TBimE ligand in **2** also adopts “cis” configuration, due to the coordination with Cd^{II}. The dihedral angle of benzimidazole rings in the TBimE ligand is 39.52°, which is larger than that of the free TBimE molecule and **1**. The bond angles around Cd atom are almost equal and from 110.16(11)° to 111.02(11)°, to result in a slightly distortable tetrahedron. The Cd-N distances are almost simlar (Cd-N(1) = 2.231(5)Å and Cd-N(3) = 2.231(4) Å, and the Cd-I bond lengths are 2.7196(7) Å and 2.7463(7)Å, respectively). The crystal packing down the *a* axis by π ••• π interactions with a face to face distance of 3.607(3) Å between the benzimidazole rings for 2 is shown in Fig. 4

IR Spectra

The infrared spectra of **1** and **2** show sharp bands in the ranges of 1605-1608 cm^{-1} and 1424-1430 cm^{-1}, attributed to ν(C = N), which is shifted slightly to lower frequency compared to the free ligand TBimE(1614 and 1434 cm^{-1}). These shifts of characteristic absorptions for TBimE indicate that the N atoms of TBimE are coordinated to metal ions. The bands at 1281 cm^{-1} for TBimE, 1287 cm^{-1} for **1** and 1283 cm^{-1} for **2** can be assigned to ν(C-N) of the TBimE ligand.

UV-vis Spectra

As shown in Fig.5, complexes **1** and **2** reveal similar transitions compared to TBimE. These results indicate that the absorptions are attributed to TBimE ligand. The absorption peaks of the complexes (**1**: 224 and 336 nm, $\varepsilon_{224} = 25700\ M^{-1}\ cm^{-1}$, $\varepsilon_{336} = 35200\ M^{-1}\ cm^{-1}$; **2**: 221 and 352 nm, $\varepsilon_{221} = 26100\ M^{-1}\ cm^{-1}$, $\varepsilon_{352} = 5800\ M^{-1}\ cm^{-1}$) are blue-shifted comparing to the ligand (222 and 362 nm, $\varepsilon_{222} = 22300\ M^{-1}\ cm^{-1}$, $\varepsilon_{362} = 31800\ M^{-1}\ cm^{-1}$), which can be owned to the effect of the coordination field of metal ion. The absorption strength at 352nm for **2** is much smaller than those of **1** and TBimE, which can also be attributed to the different coordination environment of TBimE. The two absorption bands of TBimE can be assigned to intramolecular charge transfer transitions, as a result of π→π* transitions in the ligand. The weak absorption band at 410 ~ 450 nm of TBimE is related to the n→π* transitions in TBimE molecule.

Photoluminescence

The photoluminescent properties of TBimE and complexes **1** and **2** were investigated in methanol at room temperature. TBimE and complexes exhibit similar emission band profiles (Fig. 6), which suggest that the fluorescence of **1** and **2** are a result of intraligand emission. [32] The ligand reveals a broad emission band with a peak at 426 nm (λ_{ex} = 393 nm) and complexes **1** and **2** have emission peaks at 423 nm (λ_{ex} = 400 nm) and 421 nm (λ_{ex} = 400 nm), respectively. Comparing to the free TBimE, complexes exhibit weaker emission intensity and the emission peaks have small red-shifts, which can be attributed to the coordination of TBimE molecule with metal atoms.

Conclusion

Two new complexes based on a semi-rigid ligand containing bis(2-benzimidazolyl) group, $Zn(TBimE)(Cl)_2$ (**1**) and $Cd(TBimE)(I)_2$ (**2**), have been synthesized and structurally characterized by X-ray diffraction analyses. In the structures of the complexes, TBimE ligands adopt “cis” configuration comparing to “trans” of the free TBimE, and afford two coordiantion sites to chelate metal ions, resulting in slightly distortable tetrahedral geometries. Complexes units are further linked into a 1-D chain or 2-D layer supramolecular network by hydrogen bonds and π•••π stacking interactions. The electronic absorptions and emission of **1** and **2** mainly exhibit intramolecular charge transfer transitions of the ligand.

Acknowledgements

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SUPPLEMENTARY MATERIAL

CCDC 1059527 and, CCDC 1410664 contain the supplementary crystallographic data for the complexes **1** and **2**, respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: t44-1223-336033; or e-mail: deposit@ccdc.cam.ac.uk.

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Table 1 Crystals and structures refinement data for $H_2TBimE{\bullet}Cl^{-}$, **1** and **2**

	$H_2TBimE{\bullet}Cl^{-}$	**1**	**2**
Empirical formula	$C_{16}H_{22}C_{l2}N_4O_4$	$C_{16}H_{12}Cl_2N_4Zn$	$C_{24}H_{24}CdI_2N_6$
Formula weight	405.28	396.57	762.70
Crystal system	Triclinic	Monoclinic	Monoclinic
space group	*P*-1	*P*2(1)/*n*	*P*m
a/ Å	6.098(2)	7.3175 (4)	7.2743(2)
b/ Å c/ Å	9.567(4)	15.0186(8)	16.8024(5)
α/ °	15.474(6)	14.7481 (7)	9.5824(7)
β/ °	90.887(14)	90	90
γ/ °	102.864(10)	96.9730(10)	91.0870(10)
V/ $Å^3$	82.098(3)	90	90
Z	925.8 (6)	1608.81(14)	1171.00(7)
D_c / $g{\cdot}cm^{-3}$	2	4	2
μ / mm^{-1}	1.454	1.637	2.163
R^a/wR^b	0.381	1.861	3.595
	0.2084, 0.5424	0.0732, 0.2262	0.0484, 0.1395

$^aR = \Sigma||F_o| -- |F_c||/\Sigma|F_o|$

$^bR_w = [\Sigma[w(F_o^2 -- F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$

Table 2 selected bond lengths and bond angles for 1-3

1		**2**		**3**	
N(1)-C(7)	1.35(2)	Zn-N(1)	2.001(5)	Cd-N(1)	2.231(5)
N(1)-C(1)	1.357(2)	Zn-N(3)	2.008(6)	Cd-N(1) #1	2.231(4)
N(3)-C(10)	1.35(2)	Zn-Cl(1)	2.245(2)	Cd-I(1)	2.7463(7)
C(8)-C(9)	1.37(2)	Zn-Cl(2)	2.252(2)	Cd-I(2)	2.7196(7)
C(7)-C(8)-C(9)	123.3(15)	N(1)-Zn-N(3)	104.6(2)	N(1)-Cd-N(1)#1	94.0(2)
C(8)-C(9)-C(10)	122.2(15)	N(3)-Zn-Cl(1)	115.1(2)	N(1)#1-Cd-I(2)	110.16(11)
N(3)-C(10)-C(9)	121.8(14)	N(3)-Zn-Cl(2)	111.1(2)	N(1)#1-Cd-I(1)	111.02(11)
N(4) --C(10)-C(9)	127.6(15)	N(1)-Zn-Cl(1)	109.01(17)	N(1)-Cd-I(2)	110.16(11)
N(1)-C(7)-C(8)	128.1(16)	N(1)-Zn-Cl(2)	109.01(17)	N(1)-Cd-I(1)	111.02(11)
N(2)-C(7)-C(8)	122.9(15)	Cl(1)-Zn-Cl(2)	105.54(8)	I(2)-Cd-I(1)	117.94(2)

Symmetry code : #1 *x*, -*y*+1/2, *z*

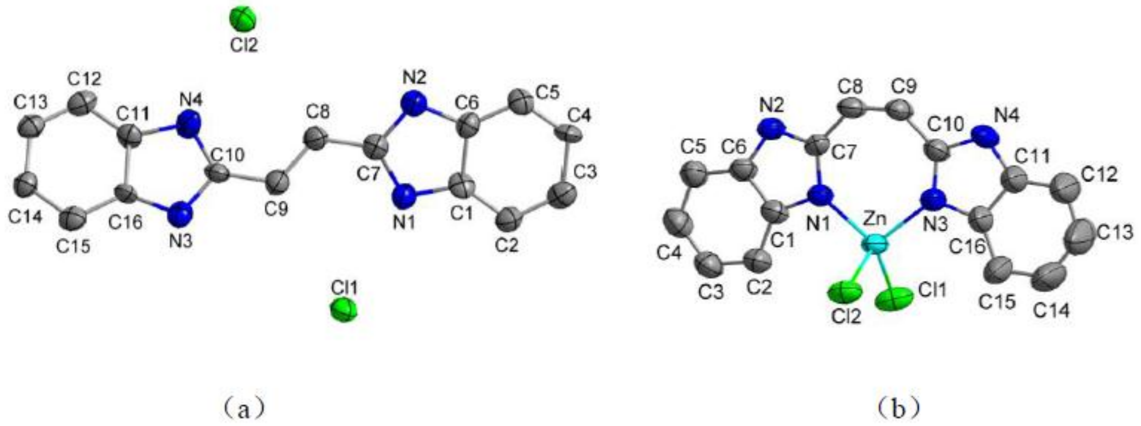

Fig. 1 Structures of $H_2TBimE•2Cl^{-}$ (a) and the complex **1** (b) at 50% probability displacement ellipsoids with atomic numbering scheme (hydrogen atoms were omitted for clarity).

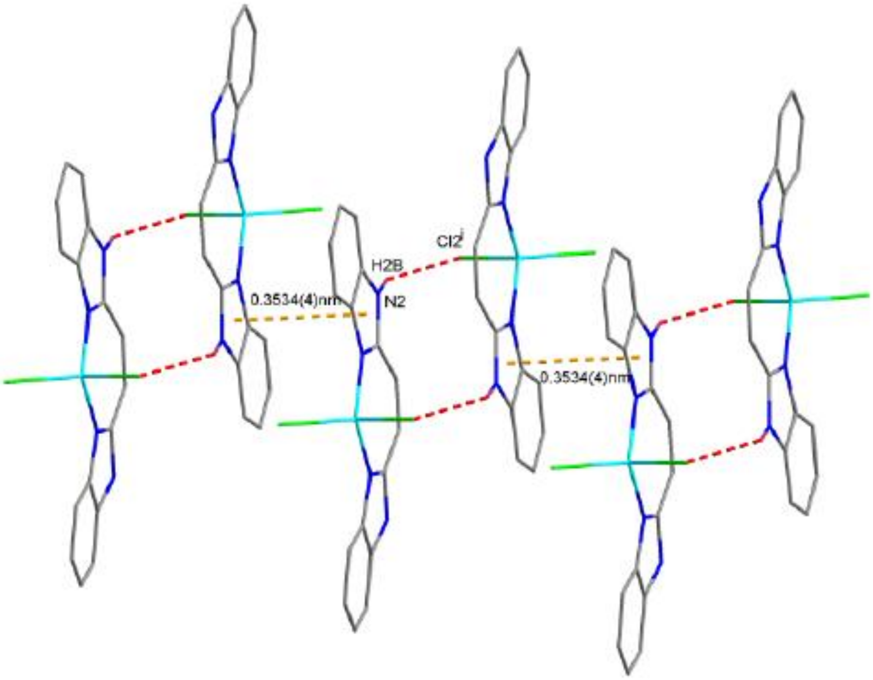

Fig. 2 1-D chain structure formed by N-H•••O and O-H•••Cl hydrogen bonds interactions in **1** (Symmetry code: i, 2-*x*, 1-*y*, 1-*z*)

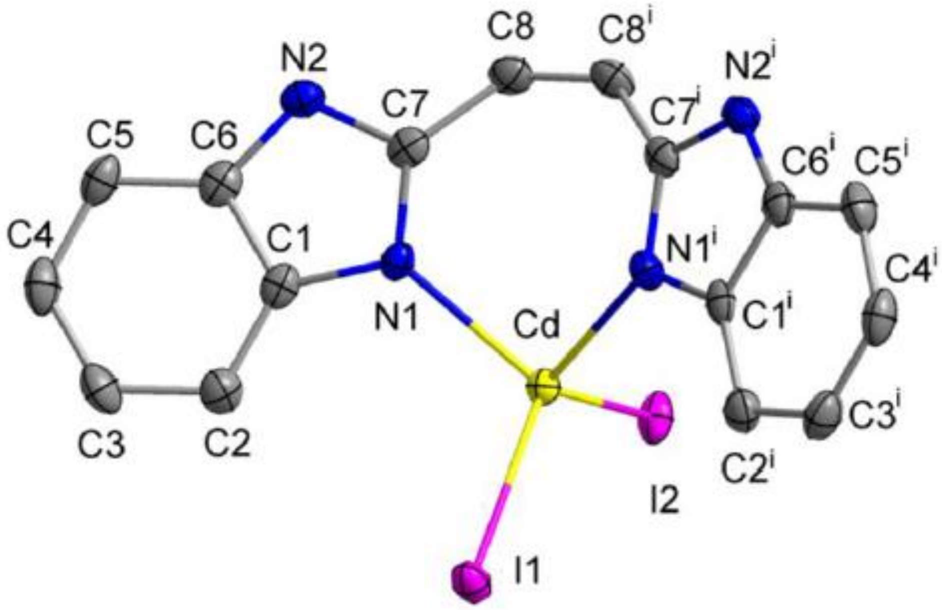

Fig. 3 Structures of 2 at 50% probability displacement ellipsoids with atomic numbering scheme (hydrogen atoms were omitted for clarity, Symmetry code: i, *x*, -*y*+1/2, *z*).

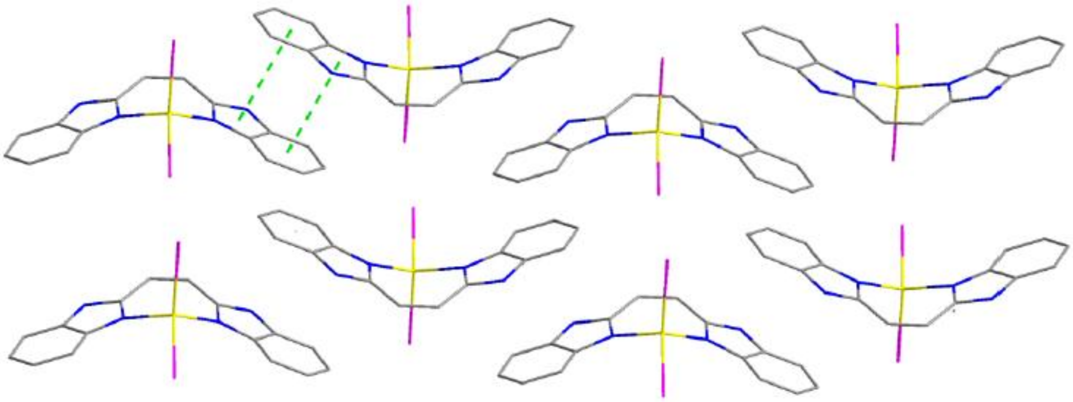

Fig.4 A view of the crystal packing down the *a* axis by π ••• π interactions for **2**

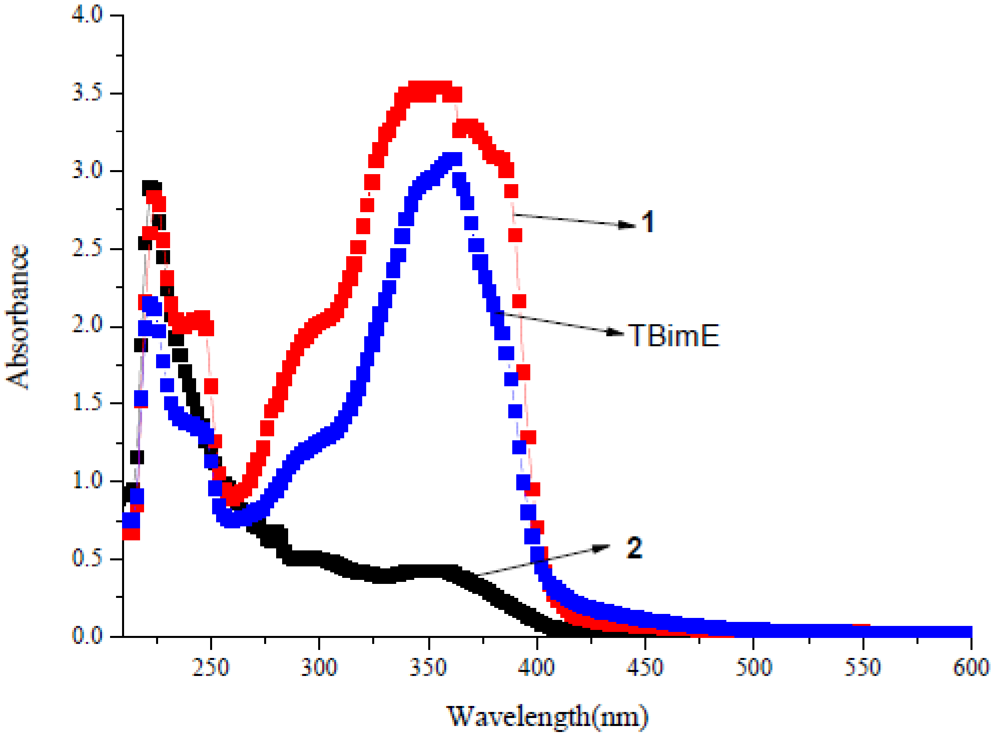

Fig. 5 UV-Vis spectra of the complexes and the TBimE ligand in methanol

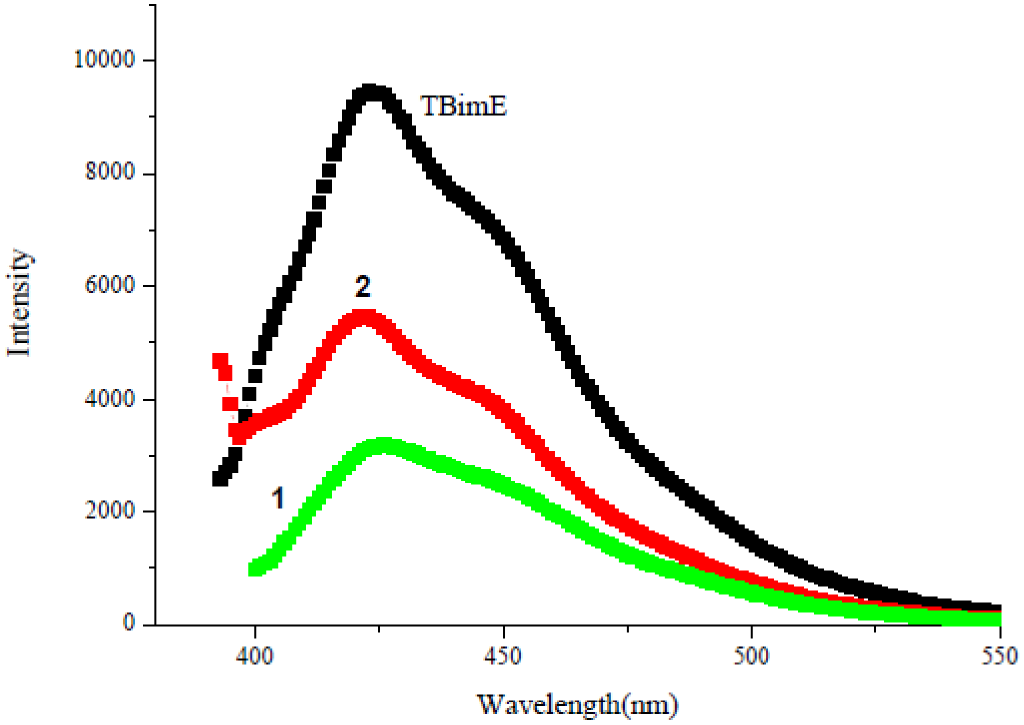

Fig. 6 Emission spectra of the TBimE and the complexes in methanol at room temperature

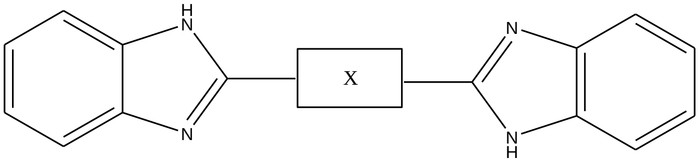

Chart 1