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Synthesis, crystal structures, and optical properties of a novel imidazole derivative and its Zn(II) complex

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Abstract

A novel imidazole derivative, 1-[*trans*-4-(4-diethylaminostyryl)phenyl]imidazole (abbreviated as L), and its complex $Zn(SCN)_2L_2$ have been synthesized and fully characterized. Their crystal structures have been determined by X-ray diffraction. The molecular structure of L is approximately coplanar, the bond lengths of C–C and C–N are located between the normal double and single bonds, which show that L has a delocalized π-electron system in the molecule. In the molecular structure of $Zn(SCN)_2L_2$, zinc atom is four coordinated by two nitrogen atoms of the ligands (L) and two nitrogen atoms of thiocyanate to form a distorted tetrahedral geometry. The one-dimensional structure of $Zn(SCN)_2L_2$ is formed by C–H···S interactions and π–π interactions. They both crystallize in the noncentrosymmetric space group $P2_1$, and exhibit powder second-harmonic generation (SHG) efficiency approximately twenty times high as that of urea, indicating promising potential applications as useful nonlinear optical (NLO) materials.

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1. Introduction

There has been intensive research on organic, metal-organic materials exhibiting second-order nonlinear optical (NLO) properties [1]. Such materials are of potential applications in electrooptic devices and second harmonic generation (SHG), which are of importance in areas such as optical communications and data storage [2–4]. Two main factors determine the NLO response of molecules. The first important factor is the requirement of noncentrosymmetric arrangement of molecules in the crystal, because the second-order susceptibility (χ^2) will vanish in a centrosymmetric environment [5,6]. However, crystallization often rarely occurs in a noncentrosymmetric space group as design. It is not possible to predict crystal geometries from molecular geometries, which has greatly hampered the progress of crystal engineering of functional solids. Therefore, design and synthesis of acentric crystals have gained scientific and technological interest [7–11]. The second factor is the requirement of delocalized π-electron system of molecules. Accordingly, the rational design and synthesis of such acentric crystal with high SHG efficiency is still a challenge to synthetic chemists and material scientists.

Moreover, the organic–inorganic hybridized coordination complexes containing imidazole derivatives, which were designed based on topologies, have been extensively reported [12], but the π-conjugated imidazole derivatives with functional group and their metal complexes, which possess excellent optical properties, are relatively scarce. Therefore, we have systematically carried out research on

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the rational design and synthesis of noncentric imidazole derivatives and their complexes containing good electron donor (D) and acceptor (A) through a conjugated bridge, which is original and different from other related reports. In this article, we report the synthesis, crystal structures, thermal stabilities, photoluminescence and SHG efficiency of a novel D-π-A structural imidazole derivative (L) and its complex $Zn(SCN)_2L_2$ with noncentrosymmetric space group.

2. Experimental

2.1. General

All commercially available chemicals are of analytical grade and used without further purification. The solvents were purified by conventional methods. 4-(Diethylamino)benzaldehyde, 4-(diethylamino)benzalcohol, and [4-(diethylamino)benzyl]triphenylphosphinium iodide were synthesized according to the methods reported [13–15]. IR spectra were recorded on a Nicolet FT-IR instrument with KBr discs in the 400–4000 cm^{-1} range. Elemental analysis was carried out on Perkin-Elmer 240 analyzer. UV–vis spectra were measured in DMF solutions (10^{-5} mol L^{-1}) with a UV-265 spectrophotometer. The solid-state luminescence spectra were recorded on a Perkin-Elmer LS55B fluorescence spectrophotometer at room temperature.

2.2. Synthesis of 4-imidazolyl-benzaldehyde

DMF (60 mL), imidazole (6.80 g, 100 mmol), anhydrous potassium carbonate (13.80 g, 100 mmol), 4-fluorobenzaldehyde (12.40 g, 100 mmol) and three drops of aliquate-336 were added to a round-bottomed flask. The reaction mixture turned yellow and was kept stirring for 24 h at 85 °C. After being cooled to room temperature, it was poured into ice-water (200 mL). The pale-yellow lamellar crystals formed immediately. The product was filtered and dried in vacuo. Yield: 90%. Anal. calcd. (%) for $C_{10}H_8N_2O$: C, 63.58; H, 5.96; N, 9.27. Found (%): C, 63.55; H, 5.94; N, 9.26. MS: $m/z = 172$.

2.3. Synthesis of 1-[trans-4-(4-diethylaminostyryl)phenyl] imidazole (L)

[4-(Diethylamino)benzyl]triphenylphosphinium iodide (5.51 g, 10 mmol), 4-imidazolyl-benzaldehyde (1.72 g, 10 mmol) and NaOH (2.00 g, 50 mmol) were placed in a mortar. The mixture was ground for 10 min, then poured into distilled water (500 mL). The product was extracted twice with CH_2Cl_2, and the organic layer was dried overnight over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give the crude product. It was purified by recrystallization from methanol. Yield: 80%. Anal. calcd. (%) for $C_{21}H_{23}N_3$: C, 79.21; H, 7.60; N, 13.20. Found (%): C, 79.19; H, 7.63; N, 13.17. ESI-MS: $m/z = 318.3$ (HM^+). IR (KBr, cm^{-1}): 3416 (m), 1601 (s), 1521 (s), 1480 (w). Single crystals of L were obtained by slow evaporation of a benzene solution at room temperature.

2.4. Synthesis of $Zn(SCN)_2L_2$

The tetrahedral zinc complex was readily prepared by layering method at room temperature. A clear methanol solution (15 mL) of $Zn(NO_3)_2 \cdot 6H_2O$ (29.80 mg, 0.1 mmol) and NaSCN (16.40 mg, 0.2 mmol) was carefully layered onto a solution of L (73.40 mg, 0.2 mmol) in chloroform (15 mL). Yellow needle-shaped crystals suitable for X-ray diffraction were obtained by slow interlayer diffusion. Yield: 70%. Anal. calcd. (%) for $ZnC_{44}H_{46}N_8S_2$: C, 64.73; H, 5.68; N, 13.77. Found (%): C, 64.78; H, 5.64; N, 13.81. IR (KBr, cm^{-1}): 3421 (m), 2073 (s), 1595 (s), 1524 (s), 1425 (w).

2.5. X-ray crystal structure determination

The X-ray diffraction measurements were performed on a Bruker SMART CCD area detector using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 298(2) K. Intensity data were collected in the variable ω-scan mode. The structures were solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed with SHELXTL-97 program package [16]. Details of the crystal parameters, data collections and refinements are listed in Table 1, and selected bond distances and angles are given in Table 2.

Table 1
Crystallographic for L and $Zn(SCN)_2L_2$

Compound	L	$Zn(SCN)_2L_2$
Empirical formula	$C_{21}H_{23}N_3$	$C_{44}H_{46}ZnN_8S_2$
Formula weight	317.42	816.38
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a (Å)	8.777(9)	19.413(3)
b (Å)	7.701(8)	10.471(1)
c (Å)	13.64(1)	21.760(3)
β (°)	106.31(2)	108.411(3)
Volume ($Å^3$)	885.0(2)	4197(1)
Z	2	4
ρ_{Calcd} (g/cm^3)	1.191	1.292
$F(000)$	340	1712
Crystal size (mm)	0.35 × 0.29 × 0.14	0.22 × 0.13 × 0.06
Reflections collected	4342	21643
Unique reflections	2659	7408
Parameters	230	496
S on F^2	1.001	1.015
R_1 [$I > 2\sigma(I)$]	0.0710	0.0508
wR_2 [$I > 2\sigma(I)$]	0.1387	0.1112
R_1	0.2165	0.1158
wR_2	0.1846	0.1423
$\Delta\rho_{min/max}$ [e. nm^{-3}]	0.0163/−0.0187	0.0517/−0.0298

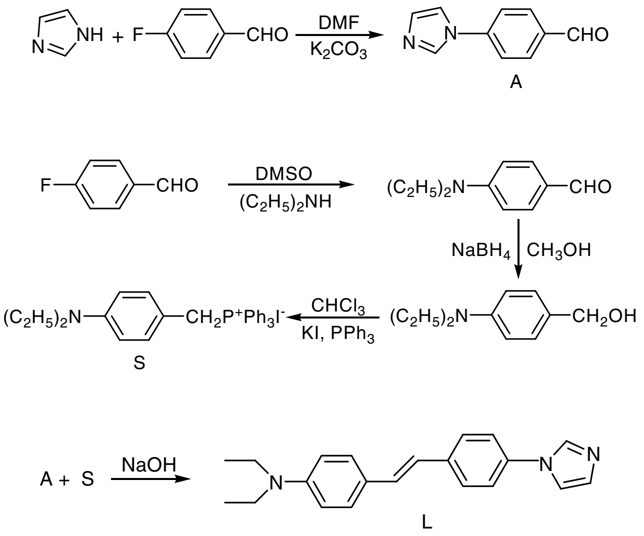
Table 2
Selected bond lengths (Å) and angles (°) for L and $Zn(SCN)_2L_2$

L			
N(3)–C(20)	1.559(12)	N(3)–C(15)	1.388(8)
N(3)–C(18)	1.573(11)	C(20)–C(21)	1.440(13)
C(18)–C(19)	1.370(12)	N(2)–C(1)	1.359(8)
N(1)–C(3)	1.355(10)	N(1)–C(1)	1.355(9)
C(2)–C(3)	1.323(9)	C(11)–C(12)	1.516(10)
N(2)–C(4)	1.397(7)	C(7)–C(10)	1.497(10)
C(2)–C(3)	1.323(9)	C(7)–C(10)	1.497(10)
C(10)–C(11)	1.168(9)	C(11)–C(12)	1.516(10)
N(2)–C(2)	1.341(9)	C(15)–N(3)–C(20)	122.2(7)
C(15)–N(3)–C(18)	122.4(7)	C(20)–N(3)–C(18)	113.6(7)
$Zn(SCN)_2L_2$			
Zn(1)–N(1)	2.007(3)	Zn(1)–N(4)	2.006(3)
Zn(1)–N(7)	1.940(4)	Zn(1)–N(8)	1.916(4)
N(1)–C(1)	1.306(4)	N(1)–C(3)	1.356(6)
N(2)–C(1)	1.327(5)	N(2)–C(2)	1.369(5)
N(2)–C(4)	1.438(4)	N(3)–C(15)	1.371(5)
N(3)–C(18)	1.442(6)	N(3)–C(20)	1.643(11)
N(4)–C(22)	1.319(5)	N(6)–C(41)	1.450(6)
N(7)–C(43)	1.150(5)	N(8)–C(44)	1.148(6)
C(2)–C(3)	1.345(6)	C(7)–C(10)	1.482(6)
C(10)–C(11)	1.261(6)	C(11)–C(12)	1.485(6)
C(12)–C(17)	1.374(6)	C(12)–C(13)	1.386(6)
C(13)–C(14)	1.398(5)	C(14)–C(15)	1.388(6)
C(15)–C(16)	1.392(6)	C(16)–C(17)	1.370(5)
N(4)–C(22)	1.319(5)	N(4)–C(24)	1.361(5)
N(5)–C(22)	1.340(5)	N(5)–C(23)	1.367(5)
N(5)–C(25)	1.430(5)	N(6)–C(36)	1.377(5)
N(6)–C(41)	1.450(6)	N(6)–C(39)	1.457(6)
C(23)–C(24)	1.342(6)	C(28)–C(31)	1.462(5)
C(32)–C(33)	1.465(5)	C(31)–C(32)	1.317(5)
C(41)–C(42)	1.503(7)	C(39)–C(40)	1.446(8)
N(8)–Zn(1)–N(7)	118.33(18)	N(8)–Zn(1)–N(4)	111.99(17)
N(7)–Zn(1)–N(4)	103.81(15)	N(8)–Zn(1)–N(1)	104.44(15)
N(7)–Zn(1)–N(1)	108.97(16)	N(4)–Zn(1)–N(1)	109.14(13)

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route of 1-[*trans*-4-(4-diethylaminostyryl)phenyl]imidazole (L) is shown in Scheme 1. It was synthesized by solvent free Wittig reaction with high yield. Wittig reaction is a widely used method to synthesize *trans*-configuration alkene. Conventional Wittig reactions are carried out in solution and in nitrogen atmosphere using strong base, such as MeONa, *t*-BuOK, NaH, $NaNH_2$, and so on. In our experiments, we ground the reaction mixture in a mortar, using the commom base – NaOH. The reaction could be accomplished within 10 min and the product could be handled easily and the yield was above 50%. Therefore, solvent free Wittig reaction is an inexpensive and convenient method to synthesize *trans*-configuration alkene.



Scheme 1. Synthesis route for L.

The IR spectrum of free L shows absorption at 1480 cm^{-1}, attributing to the vibration of the C=N of imidazole. Compared with the double peaks at 1489 and 1425 cm^{-1} assigned to the C=N of imidazole in $Zn(SCN)_2L_2$, the shift and split of the band suggests coordination of the imidazole group in the complex [17]. In the complex $Zn(SCN)_2L_2$, the strong absorption peak at 2073 cm^{-1} is for ν_{as} (NCS), which is consistent with the occurrence of thiocyanate–N coordination and agrees well with the molecular structure [18]. UV–vis spectrum of L displays absorption peak at 369 nm, which is assigned as K band absorption arising from π–π* transitions within the extended π-conjugated system [19]. The large molar absorption coefficient ($\log\varepsilon = 4.29$) is an indication of high electronic delocalization system. $Zn(SCN)_2L_2$ displays absorption peaks at 368 nm ($\log\varepsilon = 4.60$), arising from π–π* transitions of the ligands.

3.2. Crystal structures

The molecular structures of L and $Zn(SCN)_2L_2$ are shown in Figs. 1a and 2a, respectively. The selected bond distances and angles are listed in Table 2. It is important to note that, L and its complex $Zn(SCN)_2L_2$ both crystallize in the acentric monoclinic space group $P2_1$ as expected.

In the molecular structure of L, least-square plane calculations show that the dihedral angle between the two benzene rings is 9.5°, indicating they are nearly coplanar. The sum of the three C–N–C angles taking nitrogen atom as center (C(15)–N(3)–C(20), 122.2(7)°; C(18)–N(3)–C(20), 113.6(7)°; C(15)–N(3)–C(18), 122.4(7)°) is 358.2°, therefore the trigonal NC_3 is approximately coplanar. The bond lengths of N(3)–C(18) (1.57(1) Å) and N(3)–C(20) (1.56(1) Å) are longer than that of N(3)–C(15) (1.388(8) Å), confirming two electrons on N(3) are partial to the adjacent phenyl ring. It can be seen from Table 2 that all the bond lengths of C–C are located between the normal C=C double bond (1.34 Å) and C–C single bond (1.54 Å), which show that L has a highly delocalized π-electron system in the molecule. Because crystallographic disorder appears in C(10) and C(11), the bond length of C(10)–C(11) (1.168(9) Å) is shorter than the normal C=C bond length. In conclusion, the departure of C–N and the average bond

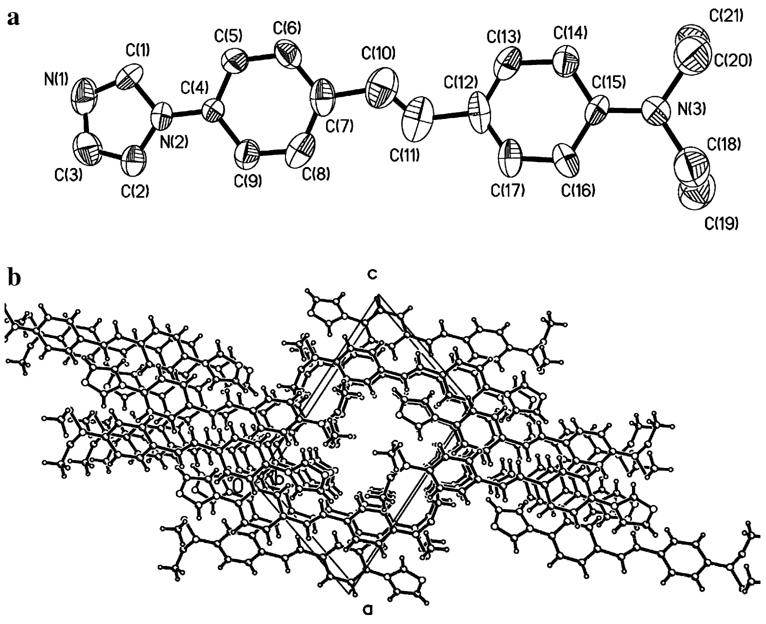


Fig. 1. (a) Molecular structure of L (hydrogen atoms are omitted for clarity). (b) Packing diagram of L.

lengths show that there is a π-conjugated system in the molecule, which is very important for the optical nonlinearities of the compound.

As shown in Fig. 2a, in the molecular structure of $Zn(SCN)_2L_2$, zinc atom is four coordinated by two nitrogen atoms of the ligands (L) and two nitrogen atoms of thiocyanate to form a distorted tetrahedral geometry. The Zn–N bond lengths are in the range between 1.914(4) Å and 2.007(3) Å. The bond angles around the zinc atom are in the range of 103.81(15)–118.33(18)°. The strong distortion in the tetrahedral environment of the four donor atoms is explained on the basis of strong stereo interactions between the ligands. The planar, corresponding bond lengths and bond angles of the two ligands (L) in the complex are different with those of the free ligand. Least-square plane calculations show that the

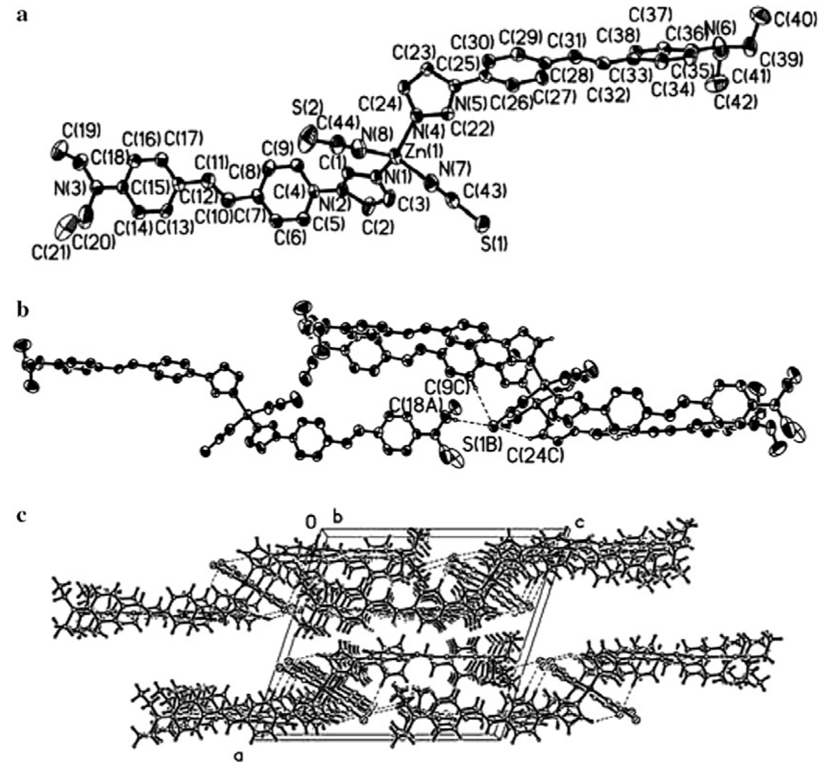


Fig. 2. (a) The Zn^{II} coordination environment in the complex of $Zn(SCN)_2L_2$ (hydrogen atoms are omitted for clarity). (b) C–H···S intermolecular interactions in crystal of $Zn(SCN)_2L_2$. (c) Perspective view of molecular packing of $Zn(SCN)_2L_2$.

dihedral angles between the two benzene rings are 3.7° (for planes containing C25, C26, C27, C28, C29, C30) and C33, C34, C35, C36, C37, C38), and 16.7° (for planes containing C25, C26, C27, C28, C29, C30 and C33, C34, C35, C36, C37, C38), respectively. While, the dihedral angle between the two benzene rings is 9.5° in the free ligand. The bond lengths and bond angles being comparable with those of free L are listed in Table 2. From Table 2, we can see that the C–C and C–N bond lengths in $Zn(SCN)_2L_2$ are more even than those of the corresponding free L. In the crystal structure, the molecules are stacked through C(9)–H(9)···S(2) (the distance of H···S is 2.871 Å and the C–H···S angle is 170.4°) and C(24)–H(24)···S(1) (the distance of H···S is 2.944 Å and the C–H···S angle is 137.5°) interactions (see Fig. 2b) along the *b* axis, to form one-dimensional structures (the van der Waals radii of H and S are 1.00 Å and 2.05 Å, respectively). The C–H···S hydrogen bond is very important in supramolecular self-assembly [20–22]. In addition to the hydrogen bonds as mentioned above, there are π–π interactions between the neighboring imidazole rings in the one-dimensional structures. The two imidazole rings from two different ligands are nearly parallel with a dihedral angle of 7.3° and a centroid-to-centroid distance of 3.802 Å. As shown in Fig. 2c, the one-dimensional chains are stacked through C(18)–H···S(1) (the distance of H···S is 2.939 Å and the C–H···S angle is 164.1°) interactions, to form a noncentrosymmetric crystal.

3.3. Thermal stability

Thermal stabilities for the imidazole derivative and its zinc complex were determined by TG technique. The TG curves exhibited that L and $Zn(SCN)_2L_2$ were stable up to their decomposition temperature of 289.3 °C and 350.6 °C, respectively, without showing any melting process, indicating the high stability of them. The decomposition temperature of $Zn(SCN)_2L_2$ is much higher than that of the free ligand. So coordination of the ligand to the metal ion results in greater thermal stability, which indicates the potential applications of $Zn(SCN)_2L_2$ due to its higher thermal stability.

3.4. Photoluminescence

The photoluminescence properties of L and $Zn(SCN)_2L_2$ were investigated in the solid state at room temperature (Fig. 3). $Zn(SCN)_2L_2$ exhibits emission band at 485 nm, which is red-shifted by 9 nm compared with that of the free ligand (L), accompanied by increased luminescent intensity. The maximum emission observed in the free ligand is assigned to the π–π* transition of the π-conjugated system, and the emission maximum of the complex is also assigned to the π–π* tentatively intraligand fluorescence due to its close resemblance to that of the free ligand. The small red shift may be a result of the above-mentioned weaker π–π interactions in the molecules of $Zn(SCN)_2L_2$ [22,23]. The photoluminescence properties indicate that the complex has more extensive of π conjugation in the system.

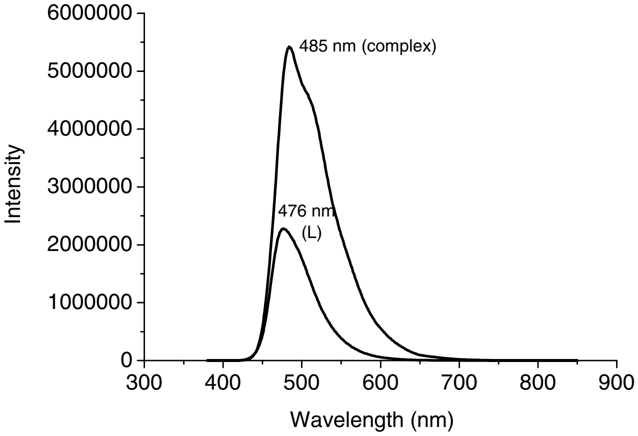


Fig. 3. The emission spectra of L and the complex $Zn(SCN)_2L_2$.

3.5. Second-order nonlinear optical properties

The imidazole derivative (L) and $Zn(SCN)_2L_2$, with noncentrosymmetric space group $P2_1$, were expected to give rise to efficient SHG effects for NLO application. Preliminary experimental results confirmed this and showed they both displayed strong powder SHG efficiencies. The SHG intensity was determined by the powder technique of Kurtz and Perry [24], in which the second harmonic output was generated by irradiating powder samples of random a Q-switched and mode-locked Nd:YAG laser. The 532 nm second harmonic intensities of L and $Zn(SCN)_2L_2$ powders were estimated as about 20 times that of NLO urea powders by direct frequency doubling of a laser diode at 1064 nm at room temperature. This result is easily understood, since the ligand in the free state and in $Zn(SCN)_2L_2$ both present extensive electron delocalization in whole system with long conjugation length between the donor and acceptor [8c]. Moreover, the solid-state electronic spectra study show that there is no absorption above 400 nm for L and $Zn(SCN)_2L_2$, which make them to be promising candidate materials for generation of blue–violet light.

4. Conclusion

A new imidazole derivative with D-π-A structure has been synthesized by solvent free Wittig reaction, and its zinc complex was obtained by self-assembly. They both possess better thermal stability. X-ray diffraction investigations reveal that they crystallize in the same noncentrosymmetric space group $P2_1$. The SHG intensities of them were observed to be much stronger than that of urea powders. In summary, the new π-conjugated imidazole derivative and its metal complex $Zn(SCN)_2L_2$ possess mechanical, thermal, chemical stabilities and excellent optical properties, which make them suitable to be used as potential NLO materials.

Acknowledgments

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Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited at the Cam-bridge Crystallographic Data Center, CCDC No. 255807 for L and CCDC No. 255805 for complex $Zn(SCN)_2L_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB221EZ, UK (fax: +44 12 23/ 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Structural factors are available on request from the authors. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2006.06.025.

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