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Synthesis, characterization and fluorescent properties of 5-(aryliminomethyl)quinaldine-8-ol derivatives and their trinuclear zinc complexes

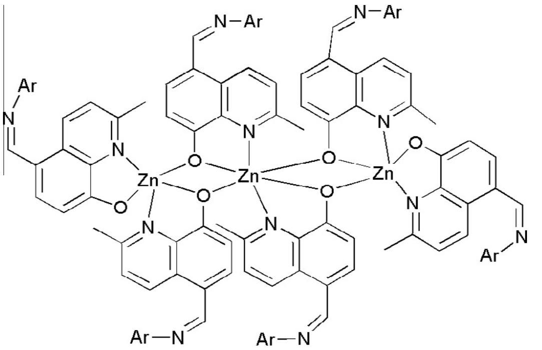
Qing Yan [a], Longlong Li [a], Wen Li [b], Lin Wang [a], Wen-Hua Sun [a,*]

[a] Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[b] Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

HIGHLIGHTS

- Newly synthesized 5-(aryliminomethyl)quinaldine-8-ol derivatives.
- Trinuclear complexes of zinc 5-(aryliminomethyl)quinaldin-8-olates.
- X-ray diffraction study on zinc complex.
- The luminescent properties enhanced through coordination.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of 5-[1-(arylimino)methyl]quinaldine-8-ol derivatives **L1**–**L5** and their trinuclear zinc(II) complexes (**C1**–**C5**) were synthesized. The compounds **L1**–**L5** were fully characterized by the FT-IR spectra, NMR measurement and elemental analysis, meanwhile the zinc complexes **C1**–**C5** were characterized by the FT-IR spectra and elemental analysis as well as the single crystal X-ray diffraction of a representative complex **C3**, which revealed a trinuclear zinc complex bearing six organic ligands. The fluorescent properties of both organic compounds and the zinc complexes have been carefully investigated by the UV–Vis absorption in various solvents, indicating the significant influences of the solvents and also double exponential decays.

Introduction

Among electroluminescent and photoluminescent materials, the metal complexes have drawn more attentions due to easy preparation and more potential applications [1–6]. Subsequence to the thermo-stable and good electroluminescence of tris(8-hydroxyquimoline)aluminum(III) (AlQ_3) [7], the 8-hydroxyquinolinyl derivatives have been extensively investigated for their aluminum complexes [8–15] and zinc complexes [16–20] as well as other metals such as gallium and indium [8,12,21–25]. In order to control the emission wavelengths and absorption strengths of compounds, there have been more efforts to adapt the various substituents on the quinolinyl ring [26–31]. Recently the zinc complexes bearing derivatives of phenol [32–34] and quinoline [35,36] showed enhanced photoluminescence, subsequently herein the 5-[1-(arylimino)methyl]quinaldine-8-ol derivatives have been synthesized and used to form their zinc complexes. Interestingly

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* Corresponding author. Tel.: +86 10 62557955; fax: +86 10 62618239.
E-mail address: whsun@iccas.ac.cn (W.-H. Sun).

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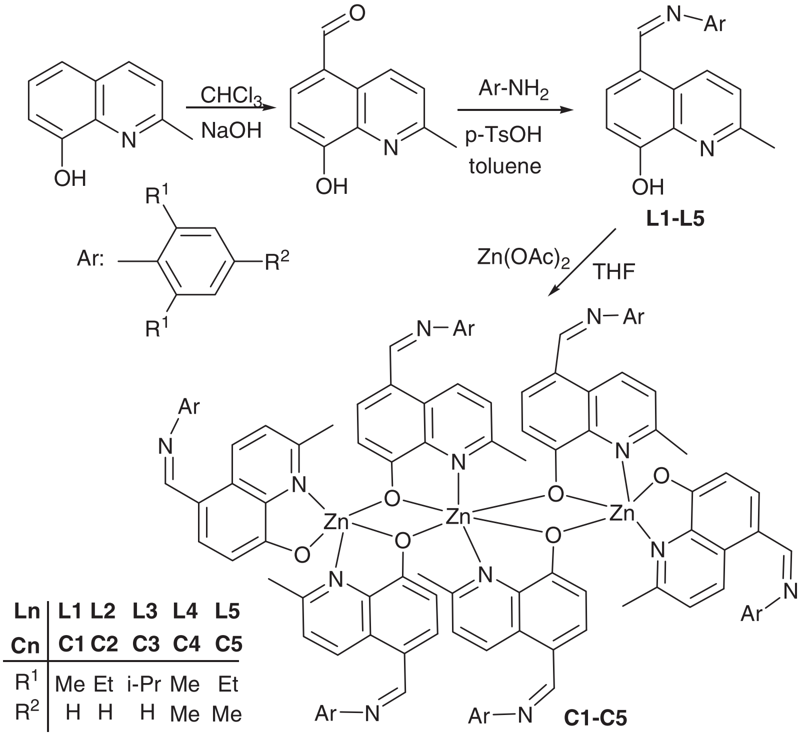

Ln	L1	L2	L3	L4	L5
Cn	C1	C2	C3	C4	C5
R^1	Me	Et	i-Pr	Me	Et
R^2	H	H	H	Me	Me

Scheme 1. Synthesis of ligands **L1**–**L5** and their zinc complexes **C1**–**C5**.

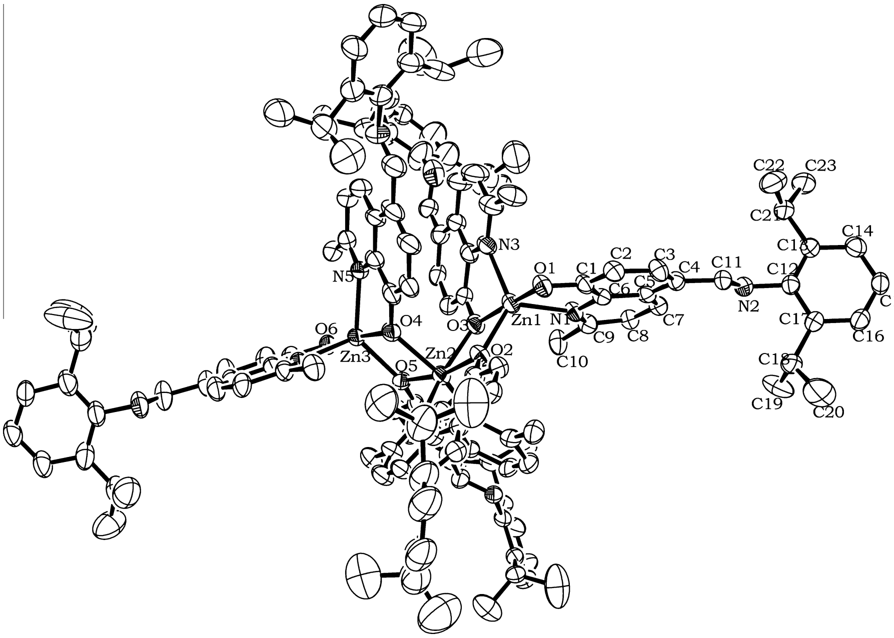

Fig. 1. ORTEP drawing of the molecular structure of **C3** (ellipsoids enclose 30% electronic density; **H** atoms were omitted for clarity).

the trinuclear complexes have been formed through coordinating three zinc with six organic ligands, and its representative complex is confirmed by the single crystal X-ray diffraction. Moreover, the photoluminescent properties of organic compounds and their zinc complexes have been extensively investigated in different solvents. The synthesis, characterization and fluorescent properties of the title compounds are reported in detail.

Results and discussion

Synthesis and characterization

The 5-formyl-8-hydroxyquinaldine was freshly prepared by the Reimer–Tiemann reaction of 8-hydroxyquinaldine [37], and further processed the condensation reaction with various anilines to

Table 1
Selected bond lengths and angles for **C3**.

Bond lengths (Å)			
Zn(1)–O(1)	1.983(4)	Zn(2)–O(5)	2.040(4)
Zn(1)–O(2)	2.072(4)	Zn(2)–N(9)	2.140(4)
Zn(1)–O(3)	2.021(4)	Zn(2)–N(11)	2.135(5)
Zn(1)–N(1)	2.143(4)	Zn(3)–O(4)	2.019(4)
Zn(1)–N(3)	2.172(5)	Zn(3)–O(5)	2.066(3)
Zn(2)–O(2)	2.026(4)	Zn(3)–O(6)	1.956(4)
Zn(2)–O(3)	2.143(4)	Zn(3)–N(5)	2.168(4)
Zn(2)–O(4)	2.143(4)	Zn(3)–N(7)	2.136(4)
Bond angles (°)			
O(1)–Zn(1)–O(3)	173.28(15)	O(5)–Zn(2)–O(4)	75.46(14)
O(1)–Zn(1)–O(2)	96.11(16)	O(5)–Zn(2)–N(9)	79.75(16)
O(1)–Zn(1)–N(1)	82.06(15)	O(5)–Zn(2)–N(11)	108.83(18)
O(1)–Zn(1)–N(3)	105.64(17)	N(9)–Zn(2)–O(3)	92.32(16)
O(2)–Zn(1)–N(1)	118.06(16)	N(9)–Zn(2)–O(4)	155.13(16)
O(2)–Zn(1)–N(3)	131.66(16)	N(11)–Zn(2)–O(3)	155.28(17)
O(3)–Zn(1)–O(2)	77.43(16)	N(11)–Zn(2)–O(4)	92.54(17)
O(3)–Zn(1)–N(1)	102.54(15)	N(11)–Zn(2)–N(9)	97.31(19)
O(3)–Zn(1)–N(3)	77.84(16)	O(6)–Zn(3)–O(4)	174.64(14)
O(1)–Zn(1)–O(3)	173.28(15)	O(6)–Zn(3)–O(5)	97.22(15)
N(1)–Zn(1)–N(3)	107.49(17)	O(6)–Zn(3)–N(7)	81.99(16)
O(2)–Zn(2)–O(3)	75.70(15)	O(6)–Zn(3)–N(5)	103.89(19)
O(2)–Zn(2)–O(4)	95.28(15)	O(5)–Zn(3)–N(7)	114.30(16)
O(2)–Zn(2)–O(5)	167.43(15)	O(5)–Zn(3)–N(5)	131.25(16)
O(2)–Zn(2)–N(9)	108.91(17)	O(4)–Zn(3)–O(5)	77.62(15)
O(2)–Zn(2)–N(11)	79.64(17)	O(4)–Zn(3)–N(7)	101.35(16)
O(4)–Zn(2)–O(3)	88.03(15)	O(4)–Zn(3)–N(5)	78.87(18)
O(5)–Zn(2)–O(3)	95.23(16)	N(7)–Zn(3)–N(5)	111.85(16)

form the 5-(aryliminomethyl)quinaldine-8-ol derivatives (**L1**–**L5**) (Scheme 1) in acceptable yields. All the organic compounds were well characterized by the FT-IR spectra and NMR measurements, and their elemental analyses were well consistent to their molecular formula.

These 5-(aryliminomethyl)quinaldine-8-ol derivatives individually reacted with half-equivalent mole of zinc acetate in tetrahydrofuran (THF) at room temperature; in the light of adding petroleum ether to concentrated THF solution, the precipitated yellow solids as their zinc complexes were collected in good yields. These zinc complexes were characterized by the FT-IR spectra and the elemental analysis. To confirm their absolute structure, the single crystals of complexes **C3** were isolated and characterized by the single-crystal X-ray diffraction method.

Molecular structure

Single crystals of complex **C3** suitable for X-ray diffraction analyses were obtained from its dichloromethane solution on layering with *n*-heptane at room temperature. The complex **C3** is a trinuclear zinc(II) complex, in which three zinc atoms are bridged by six oxo-atoms of 8-oxy-5-iminoquinaldinyl ligands; two zinc atoms (Zn1 and Zn3) are five-coordinated with three oxo-atoms and two nitrogen atoms meanwhile the middle zinc (Zn2) atom is six-coordinated with four oxo-atoms and two nitrogen atoms. Its molecular structure is illustrated in Fig. 1, and the selected bond lengths and angles are tabulated in Table 1. It is worthy to mention that there are no direct zinc–zinc bonds with the Zn1–Zn2 length 3.240 Å and the Zn2–Zn3 length 3.243 Å as well as the angle of Zn1–Zn2–Zn3 113°.

Six ligands in the complex **C3** are not interacted to each other, and the quinaldinylimino-aryl groups have been stretched far out from zinc cores. There is no observation of the imino-coordination within such complex.

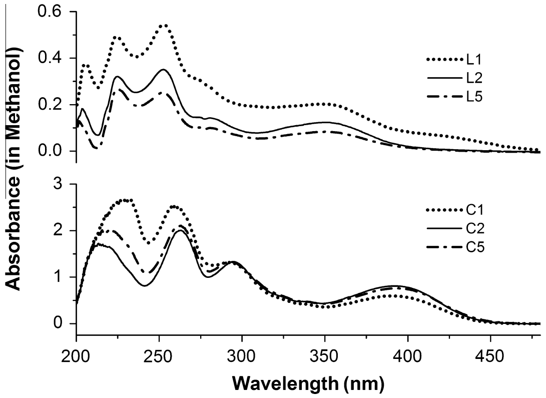

Fig. 2. UV–Vis absorption spectra of ligands (**L1**, **L2**, **L5**) and zinc complexes (**C1**, **C2**, **C5**) in methanol.

UV–Vis absorption

To understand the fluorescent properties of the 5-(aryliminomethyl)quinaldine-8-ol derivatives and their zinc complexes, their UV–Vis absorption spectra have been measured in the solvent such as methanol, THF or toluene with fixing the solution concentration as 1×10^{-5} M. Their data are tabulated in Table 2.

In the typical polar solvent of methanol, the highly similar curves with four absorption peaks were observed; for example, the organic compounds (**L1**, **L2**, **L5**) showed absorptions at around 205, 220, 246 and 339 nm in comparison to their Zn complexes (**C1**, **C2**, **C5**) observed at around 228, 260, 296 and 392 nm, being illustrated in Fig. 2. In the light of effective coordination between

Table 2
The UV–Vis absorption of ligands and their zinc complexes.

Solvent	Ligands	$\lambda_{\text{abs-max}}$ (nm)	$\varepsilon_{(\lambda\text{max})}$ (M^{-1} cm^{-1})	Complex	$\lambda_{\text{abs-max}}$ (nm)	$\varepsilon_{(\lambda\text{max})}$ (M^{-1} cm^{-1})
Methanol	**L1**	247	54,580	**C1**	230	2,67,960
THF		248	24,590		268	1,79,470
Toluene		284	22,920		286	87,380
Methanol	**L2**	247	34,890	**C2**	263	2,01,430
THF		248	31,430		269	2,34,740
Toluene		284	19,830		300	1,59,440
Methanol	**L3**	217	1,83,100	**C3**	262	2,24,980
THF		277	13,090		269	2,05,850
Toluene		284	22,320		300	1,43,430
Methanol	**L4**	247	34,550	**C4**	222	1,42,660
THF		248	23,310		269	2,32,920
Toluene		284	29,840		286	72,330
Methanol	**L5**	222	26,430	**C5**	262	2,10,190
THF		250	23,410		270	2,43,380
Toluene		284	17,360		300	1,45,790

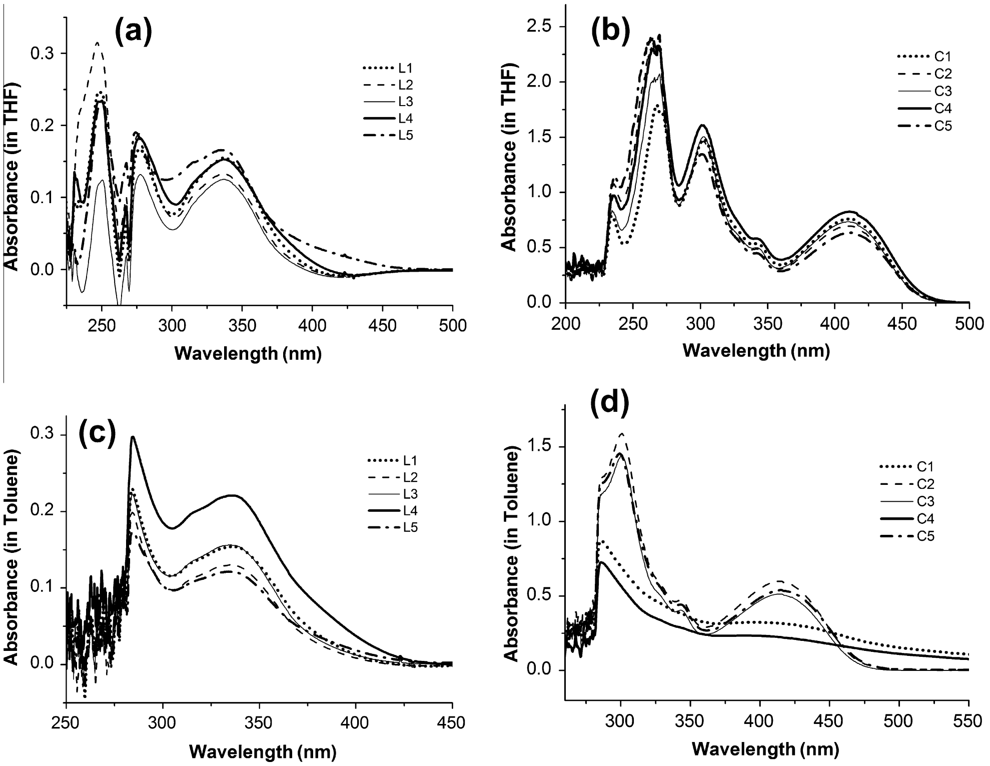

Fig. 3. (a) Absorption spectra of **L1**–**L5** in THF; (b) absorption spectra of **C1**–**C5** in THF; (c) absorption spectra of **L1**–**L5** in toluene; (d) absorption spectra of **C1**–**C5** in toluene.

Table 3
Emission data for compounds **L1**–**L5** and **C1**–**C5**.

Solvent		Ligands				Complexes		
		λ_{maxEm} (nm)	λ_{Ex} (nm)	$\Delta\lambda^a$ (nm)		λ_{maxEm} (nm)	λ_{Ex} (nm)	$\Delta\lambda^a$ (nm)
Methanol	**L1**	337	225	112	**C1**	330	284	46
THF		327	277	50		335	284	51
Toluene		329	291	38		332	293	39
Methanol	**L2**	340	226	114	**C2**	342	233	109
THF		327	279	48		334	284	50
Toluene		330	291	39		334	291	43
Methanol	**L3**	333	224	109	**C3**	347	236	111
THF		325	279	46		331	284	47
Toluene		328	290	38		335	291	44
Methanol	**L4**	335	224	111	**C4**	343	235	108
THF		327	277	50		332	284	48
Toluene		328	290	38		332	293	39
Methanol	**L5**	339	226	113	**C5**	343	236	107
THF		284	262	22		333	285	48
Toluene		328	293	35		335	290	45

[a] $\Delta\lambda$ = Stokes shift.

zinc atoms and organic compounds, their complexes significantly displayed stronger absorptions with red shifts to their organic analogs.

Subsequently, their UV-absorption were also investigated in non-polar solvent such as THF or toluene in Fig. 3. All the organic compounds (**L1**–**L5**) exhibited maximum absorption peaks at around 248 nm in THF (Fig. 3a) and 284 nm in toluene (Fig. 3c); meanwhile all the zinc complexes (**C1**–**C5**) showed at around 268 nm in THF (Fig. 3b) and 300 nm in toluene (Fig. 3d). There were clearly red-shifted absorptions observed in their THF solutions than those of toluene solutions, about 36 nm for the organic compounds (**L1**–**L5**) and 32 nm for the zinc complexes (**C1**–**C5**). Similar to the observations in their methanol solutions, the absorption strengths of all the zinc complexes (**C1**–**C5**) were enhanced along with red-shifts in comparison to the peaks of their corresponding ligands.

On the base of above data, the absorptions of both organic and its complex were significantly affected by the solvent. In general, the maximum absorptive wavelengths ($\lambda_{abs\text{-}max}$) of all the ligands and their corresponding complexes exhibited blue-shifts along with either incorporation of oxo-solvents or higher polarity of the solvents, which were consistent to the energy gap (ΔE) enlarged with increasing the polarity of the solvent used [34,38,39].

Fluorescent properties

Fixed the solution concentration at 1×10^{-5} M, the emission data of all the organic compounds and their zinc complexes were measured in the solvents of methanol, THF and toluene,

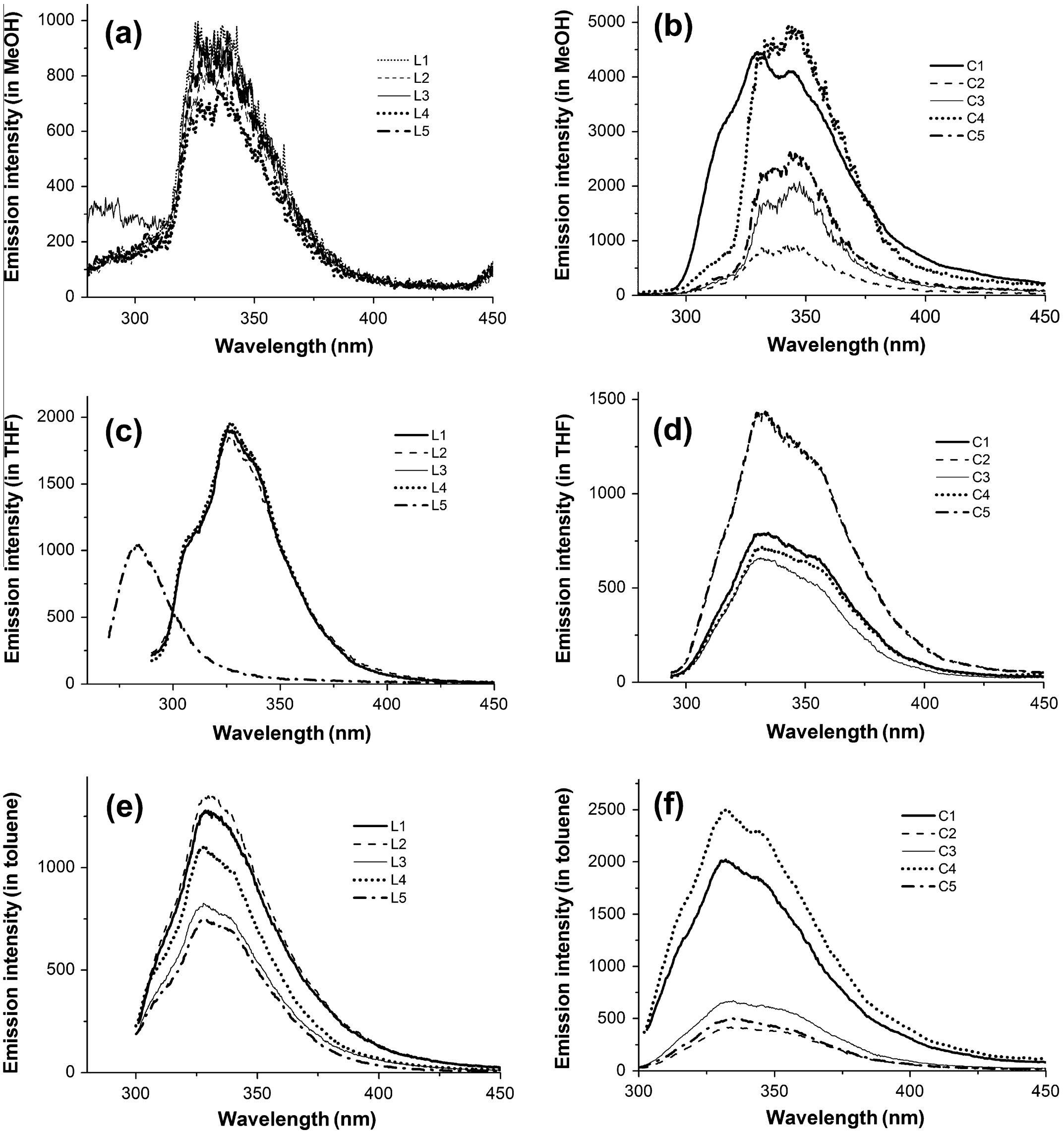

Fig. 4. Fluorescence spectra of ligands **L1**–**L5** and zinc complexes **C1**–**C5** in different solvents: (a and b) methanol; (c and d) THF; (e and f) toluene.

Table 4
Excited singlet state lifetimes (τ) and the values of radiative decay rate (k_r) of ligands (**L1**–**L5**) and zinc complexes (**C1**–**C5**).

		Ligands						Complexes				
Solvent		Φ_s	τ_1 (ns)	k_{r1}[a] (10^6 s^{-1})	τ_2 (ns)	k_{r2}[a] (10^6 s^{-1})		Φ_s	τ_1 (ns)	k_{r1}[a] (10^6 s^{-1})	τ_2 (ns)	k_{r2}[a] (10^6 s^{-1})
Methanol	**L1**	0.1052	7.882	13.34	1.695	62.04	**C1**	0.1124	9.813	11.45	1.675	67.09
Methanol	**L2**	0.1435	8.490	16.91	1.917	74.87	**C2**	0.6795	9.452	71.89	1.873	362.8
Methanol	**L3**	0.0338	11.16	3.031	2.131	15.87	**C3**	0.0427	10.62	4.022	2.132	20.04
Methanol	**L4**	0.1319	9.155	14.40	1.197	110.2	**C4**	0.1878	10.49	17.09	1.213	154.8
Methanol	**L5**	0.2027	12.00	16.89	1.886	107.5	**C5**	0.0579	10.01	5.780	1.523	37.99
THF	**L2**	0.3543	15.52	22.83	4.432	79.95	**C2**	0.0435	7.673	5.667	3.806	11.42
Toluene	**L2**	0.4940	10.13	48.77	3.230	152.9	**C2**	0.0214	8.209	2.609	2.326	9.207

Concentration: 1×10^{-5} M.

[a] $k_r = \Phi_F/\tau$.

individually, and their data are collected in Table 3. All the organic compounds and their zinc complexes exhibited large Stokes shift in methanol, however, small Stokes shifts appeared in the non-polar solvents of THF and toluene. For example, the Stokes shifts ($\Delta\lambda$) for compound **L3** is 109 nm in methanol, 46 nm in THF and 38 nm in toluene; whilst the Stokes shifts for complex **C3** are 111 nm in methanol, 47 nm in THF and 44 nm in toluene. The potential of the hydrogen bond between methanol and compounds caused the large Stokes shift [33,36]. By verifying solvents, the similar Stokes shifts were observed with the solution of both organic compounds **L1**–**L5** and their corresponding zinc complexes **C1**–**C5**.

Their fluorescence spectra are showed in Fig. 4. In methanol, compounds **L1**–**L5** showed similar curves, and the maximum emission wavelengths (λ_{maxEm}) were close between organic compound

Table 5
Summary of crystallographic data for **C3**.

C3	
Empirical formula	$C_{138}H_{150}N_{12}O_6Zn_3$
Formula weight	2268.81
Crystal color	Black
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 21/C
a (Å)	16.873(3)
b (Å)	46.679(9)
C (Å)	18.366(4)
α (°)	90
β (°)	104.87(3)
γ (°)	90
Volume (Å^3)	13981(5)
Z	4
D calcd (mg m^{-3})	1.078
μ (mm^{-1})	0.580
F (000)	4800
Crystal size (mm)	0.51 × 0.21 × 0.20
θ range (°)	1.44–25.00
Limiting indices	$-19 \leqslant h \leqslant 19$ $-54 \leqslant k \leqslant 55$ $-21 \leqslant l \leqslant 21$
No. of rflns collected	70,964
No. of unique rflns	24,472
R_{int}	0.0528
Completeness to θ (%)	99.4 (θ = 25.00)
Goodness-of-fit on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0983$ $wR2 = 0.2781$
R indices (all data)	$R1 = 0.1203$ $wR2 = 0.2997$
Largest diff. peak and hole (e Å^{-3})	1.259 and −0.681

and their zinc complex. For example, the λ_{maxEm} for compounds **L1**–**L5** were 337, 340, 333, 335, 339 nm, respectively; whilst the λ_{maxEm} for complexes **C1**–**C5** were 330, 342, 347, 343, 343 nm, respectively. The tendency of observed data was similar in other solvents, however, different fluorescence intensities were observed, indicating the substituent effect on the fluorescence spectra. As a fact, the verified substituents are not centred in the molecules, and their causes are not understood and waiting for further investigation.

The fluorescence quantum yields, excited singlet state lifetimes (τ) and the values of radiative decay rate (k_r) are tabulated in Table 4. In methanol, the quantum yield of all the ligands were observed to be in the order **L5** > **L2** > **L4** > **L1** > **L3**. However, for the complexes, the quantum yield of complex **C2** is significantly higher than those of other complexes with the order **C2** > **C4** > **C1** > **C5** > **C3**. In general, the fluorescent quantum yields of their corresponding zinc complexes were enhanced to some extent, this is described to the newly formed rings through the coordination of zinc and the ligands and leading to bigger and more rigid structures. Therefore the interaction between the excited molecules and solvent molecules were reduced to result the reducing of energy transfer, which could be beneficial to the fluorescence emission. In using THF or toluene as the solvent, the fluorescence of complex **C2** was significantly quenched in the comparison to organic **L2**. In addition, the fluorescence decay of all organic compounds and zinc complexes followed a double exponential decay in various solvents, probably due to two π-conjugated rings existed.

Conclusion

A series of 5-[1-(arylimino)methyl]quinaldine-8-ol derivatives **L1**–**L5** and their Zn(II) complexes (**C1**–**C5**) were synthesized and full characterized. The molecular structure of **C3** was confirmed as the trinuclear complex by the single-crystal X-ray diffraction. The UV-absorption spectra and Fluorescence properties of all the compounds were investigated in the solvents such as methanol, THF and toluene. The maximum UV-absorptions of both organic compounds and their zinc complexes exhibited red-shifts in toluene. In methanol, the fluorescent quantum yields of their corresponding zinc complexes were enhanced. With comparative study of compounds **L2** and **C2**, the maximum fluorescent quantum yields of complex **C2** were quenched in toluene and THF. All the organic compounds and zinc complexes exhibited double exponential decays in various solvents, attributing to the two π-conjugated rings in their molecular structures.

Experimental

General consideration

All manipulations of air and/or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. THF was refluxed over sodium–benzophenone and distilled under nitrogen prior to use. IR spectra were recorded on a Perkin Elmer FT-IR 2000 spectrometer in the range of 4000–400 cm^{-1}. Elemental analysis was performed on a Flash EA 1112 microanalyzer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. The steadystate fluorescent spectra were measured on an F4500-FL fluorescence spectrophotometer; fluorescence lifetimes were obtained using the time-correlated single-photon counting technique (Edinburgh Analytical Instruments F900 fluorescence spectrofluorimeter). Thin films of the samples were prepared on quartz slides (1 cm) through spin-coating. The fluorescence quantum yield for samples in solution was measured by using the solution containing coumarin 307 in methanol ($\Phi_r = 0.56$) standard as the reference, Φ was calculated according to the following equation: [36,40].

$$\Phi_s = \Phi_r\left(\frac{A_r(\lambda_r)}{A_s(\lambda_s)}\right)\left(\frac{I(\lambda_r)}{I(\lambda_s)}\right)\left(\frac{n_s^2}{n_r^2}\right)\frac{\int F_s}{\int F_r}$$

where r represents the standard, s represents the samples, A_r (λ_r) and A_s (λ_s) are the respective absorbance of the standard and the measured samples, I (λ_r) and I (λ_s) are the respective emission intensities of the standards and samples, n is the refractive index of the corresponding solvents, $\int F$ is the integral area of one-photon fluorescence, and Φ represents the fluorescence quantum yield.

*Synthesis of 5-[1-(arylimino)methyl]quinaldine-8-ol derivatives (**L1**–**L5**)*

*2-Methyl-5-(1-(2,6-dimethylphenylimino)methyl)quinolin-8-ol (**L1**).* A solution of 8-hydroxyquinaldine-5-carbaldehyde (1.87 g, 10 mmol) and 2,6-dimethylbenzenamine (1.45 g, 12 mmol) and a catalytic amount of p-toluenesulfonic acid in toluene (150 mL) was refluxed for 12 h, then the solvents was evaporated at reduced pressure. The product, 2-methyl-5-(1-(2,6-dimethylphenylimino)methyl)quinolin-8-ol (**L1**), was purified by column chromatography (silica gel, $V_{petroleum\ ether}$:$V_{ethyl\ acetate}$ = 30:1), and was a yellow powder, which was collected in 26.6% (0.77 g). ^{1}H NMR (400 MHz, CDCl$_3$, ppm):δ 9.90 (d, J = 8.0 Hz, 1H), 8.48 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.8 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 7.6 Hz, 2H), 6.98 (d, J = 7.6 Hz, 1H), 2.80 (s, 3H), 2.20 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 163.3, 157.4, 154.7, 151.9, 137.9, 135.4, 134.0, 128.2, 127.3, 125.2, 124.4, 123.7, 122.6, 109.1, 24.9, 18.6. FT-IR (cm^{-1}): 3295 (m), 2981 (w), 2914 (w), 1637 (m), 1608 (m), 1590 (m), 1564 (s), 1503 (s), 1472 (m), 1431 (w), 1410 (w), 1369 (m), 1330 (m), 1269 (m), 1253 (w), 1234 (w), 1194 (m), 1150 (m), 1087 (m), 982 (m), 836 (s), 799 (s), 760 (s), 713 (s). Anal. Calcd. For $C_{19}H_{18}N_2O$ (290.36): C, 78.59; H, 6.25; N, 9.65. Found: C, 78.28; H, 6.33; N, 9.59%.

*2-Methyl-5-(1-(2,6-diethylphenylimino)methyl)quinolin-8-ol (**L2**).* Using the same procedure as for the synthesis of **L1**, but 2,6-diethylbenzenamine was used instead of 2,6-dimethylbenzenamine. The 2-methyl-5-(1-(2,6-diethylphenylimino)methyl)quinolin-8-ol was obtained as a yellow solid in 44.9% (1.43 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.93 (bs, 1H), 8.49 (s, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 7.6 Hz, 2H), 7.06 (d, J = 7.6 Hz, 1H), 2.82 (s, 3H), 2.56 (m, 4H), 1.16 (t, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.9, 157.4, 154.7, 151.1, 137.9, 135.3, 134.1, 133.3, 126.5, 125.2, 124.5, 123.9, 122.5, 109.1, 25.0, 24.9, 14.9. FT-IR (cm^{-1}): 3305 (m), 2964 (w), 2868 (w), 1639(m), 1608 (s), 1563 (s), 1503 (s), 1447 (m), 1369 (w), 1331 (w), 1261 (w), 1224 (s), 1186 (w), 1155 (s), 1097 (w), 1046 (w), 904 (w), 837 (s), 792 (m), 749 (s), 710 (m). Anal. Calcd. For $C_{21}H_{22}N_2O$ (318.17): C, 79.21; H, 6.96; N, 8.80. Found: C, 78.89; H, 6.90; N, 8.76%.

*2-Methyl-5-(1-(2,6-diisopropylphenylimino)methyl)quinolin-8-ol (**L3**).* Using the same procedure as for the synthesis of **L1**, but 2,6-diisopropylbenzenamine was used instead of 2,6-dimethylbenzenamine. The 2-methyl-5-(1-(2,6-diisopropylphenylimino)methyl) quinolin-8-ol was obtained as a yellow solid in 56.2% (1.94 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ9.80 (d, J = 8.8 Hz, 1H), 8.48 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.8 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 7.6 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 3.10–3.03 (m, 2H), 2.77 (s, 3H), 1.19 (d, J = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.7, 157.4, 154.7, 150.0, 137.8, 135.3, 134.0, 125.2, 124.5, 124.1, 123.2, 122.5, 109.2, 28.2, 24.9, 23.6. FT-IR (cm^{-1}): 3310 (m), 2961 (m), 1637 (m), 1612 (s), 1563 (s), 1506 (s), 1468 (w), 1363 (w), 1327 (m), 1262 (s), 1223 (m), 1183 (w), 1156 (m), 1101 (w), 1077 (w), 1049 (m), 903 (w), 842 (s), 789 (m), 745 (s), 711 (s). Anal. Calcd. For $C_{23}H_{26}N_2O$ (346.47): C, 79.73; H, 7.56; N, 8.09. Found: C, 79.73; H, 7.75; N, 8.05%.

*2-Methyl-5-(1-(2,4,6-trimethylphenylimino)methyl)quinolin-8-ol (**L4**).* Using the same procedure as for the synthesis of **L1**, but 2,4,6-trimethylbenzenamine was used instead of 2,6-dimethylbenzenamine. The 2-methyl-5-(1-(2,4,6-trimethylphenylimino) methyl) quinolin-8-ol was obtained as a yellow solid in 30.3% (0.92 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.83 (d, J = 8.4 Hz, 1H), 8.48 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.8 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 6.93 (s, 2H), 2.76 (s, 3H), 2.31 (s, 3H), 2.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 163.3, 157.3, 154.6, 149.5, 137.9, 135.4, 133.7, 132.9, 128.9, 127.2, 125.1, 124.3, 122.7, 109.0, 24.9, 20.8, 18.5. FT-IR (cm^{-1}): 3305 (m), 2913 (w), 2846 (w), 1639 (m), 1605 (s), 1563 (s), 1506 (m), 1474 (m), 1372 (w), 1331 (w), 1266 (m), 1199 (m), 1170 (w), 1142 (s), 1031 (m), 834 (s), 797 (w), 710 (m). Anal. Calcd. For $C_{20}H_{20}N_2O$ (304.39): C, 78.92; H, 6.62; N, 9.20. Found: C, 78.77; H, 6.62; N, 9.07%.

*2-Methyl-5-(1-(2,6-diethyl-4-methylphenylimino)methyl)quinolin-8-ol (**L5**).* Using the same procedure as for the synthesis of **L1**, but 2,6-diethyl-4-methylbenzenamine was used instead of 2,6-dimethylbenzenamine. The 2-methyl-5-(1-(2,6-diethyl-4-methyl phenylimino)methyl)quinolin-8-ol was obtained as a yellow solid in 44.1% (1.46 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.89 (bs, 1H), 8.47 (s, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 8.8 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 6.94 (s, 2H), 2.80 (s, 3H), 2.55–2.48 (m, 4H), 2.34 (s, 3H), 1.15 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 163.0, 157.4, 154.6, 148.7, 137.9, 135.4, 133.9, 133.3, 133.2, 127.2, 125.2, 124.5, 122.7, 109.1, 25.0, 24.9, 21.1, 15.0. FT-IR (cm^{-1}): 3311 (m), 2966 (m), 2927 (w), 2870 (w), 1638 (m), 1614 (s), 1566 (s), 1503 (s), 1460 (w), 1371 (w), 1331 (w), 1268 (s), 1236 (w), 1199 (s), 1169 (m), 1139 (s), 1078 (w), 1049 (w), 882 (m), 839 (s), 800 (s), 714 (s). Anal. Calcd. For $C_{22}H_{24}N_2O$ (332.44): C, 79.48; H, 7.28; N, 8.43. Found: C, 79.16; H, 7.39; N, 8.39%.

*The synthesis of the zinc complexes (**C1–C5**)*

*The synthesis of complex **C1*** To a THF solution (6 ml) of 0.29 g (1.00 mmol) 2-methyl-5-(1-(2,6-dimethylphenylimino)methyl) quinolin-8-ol (**L1**), then an ethanol solution (4 ml) of 0.11 g (0.50 mmol) zinc acetate dehydrate was added. The reaction mixture was stirred at room temperature for 18 h. Then the solvent was removed under vacuum, and petroleum ether was added to precipitate the complex. The resulting precipitate was filtered, washed with petroleum ether, and dried under vacuum to furnish the product **C1** as a yellow powder in 67.6% (0.22 g) yield. FT-IR (cm^{-1}): 3079 (w), 1629 (s), 1604 (s), 1578 (s), 1514 (s), 1467 (w), 1433 (w), 1376 (m), 1345 (s), 1315 (s), 1249 (w), 1226 (m), 1202 (m), 1174 (s), 1104 (m), 1066 (m), 981 (w), 857 (w), 838 (s), 799 (m), 754 (s), 734(m). Anal. Calcd. For $C_{114}H_{102}N_{12}O_6Zn_3$ (1932.28): C, 70.86; H, 5.32; N, 8.70. Found: C, 70.68; H, 5.35; N, 8.56%.

*The synthesis of **C2*** Using the same procedure as for the synthesis of **C1**, **C2** was prepared by using **L2** instead of **L1** and a yellow powder was obtained in 68.2% (0.24 g) yield. FT-IR (cm^{-1}): 2971 (m), 2932 (w), 1629 (s), 1603 (s), 1557 (s), 1513 (s) 1455 (s), 1378 (w), 1345 (m), 1312 (s), 1220 (m), 1169 (s), 1105 (m), 1063 (m), 861 (w), 835 (s), 797 (s), 747.1 (s). Anal. Calcd. For $C_{126}H_{126}N_{12}O_6Zn_3$ (2100.6): C, 72.04; H, 6.05; N, 8.00. Found: C, 72.25; H, 6.14; N, 7.83%.

*The synthesis of **C3*** Using the same procedure as for the synthesis of **C1**, **C4** was prepared by using **L3** instead of **L1** and a yellow powder was obtained in 84.5% (0.093 g) yield. FT-IR (cm^{-1}): 2958 (m), 2865 (w), 1628 (m), 1604 (m), 1552 (s), 1513 (s), 1454 (s), 1378 (w), 1336 (w), 1305 (s), 1219 (m), 1166 (s), 1099 (s), 1058 (m), 914 (w), 836 (m), 792 (m), 733 (m). Anal. Calcd. For $C_{138}H_{150}N_{12}O_6Zn_3$ (2268.91): C, 73.06; H, 6.66; N, 7.41. Found: C, 73.01; H, 6.62; N, 7.33%.

*The synthesis of **C4*** Using the same procedure as for the synthesis of **C1**, **C4** was prepared by using **L4** instead of **L1** and a yellow powder was obtained in 90.6% (0.15 g) yield. FT-IR (cm^{-1}): 2916 (w), 2857 (w), 1631 (s), 1601 (s), 1556 (s), 1513 (s), 1433 (s), 1374 (w), 1344 (m), 1312 (m), 1203 (w), 1180 (w), 1139 (w), 1100 (w), 1065 (w), 1033 (w), 836 (m), 797 (w). Anal. Calcd. For $C_{120}H_{114}N_{12}O_6Zn_3$ (2016.44): C, 71.48; H, 5.70; N, 8.34. Found: C, 71.32; H, 5.68; N, 8.29%.

*The synthesis of **C5*** Using the same procedure as for the synthesis of **C1**, **C5** was prepared by using **L5** instead of **L1** and a yellow powder was obtained in 76.7% (0.084 g) yield. FT-IR (cm^{-1}): 2973 (w), 1628 (m), 1601 (m), 1560 (s), 1513 (s), 1460 (m), 1376 (m), 1348 (m), 1316 (s), 1273 (w), 1227 (w), 1206 (m), 1185 (m), 1160 (w), 1141 (m), 1105 (m), 1063 (m), 990 (w), 862 (m), 837 (s), 797 (m), 740 (m). Anal. Calcd. For $C_{132}H_{138}N_{12}O_6Zn_3$ (2184.75): C, 72.57; H, 6.37; N, 7.69. Found: C, 72.68; H, 6.42; N, 7.68%.

X-ray diffraction study

Single crystals of complex **C3** suitable for single-crystal X-ray analysis were obtained by laying *n*-heptane on the dichloromethane solutions. Single-crystal X-ray diffraction for complex **C3** were performed on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173(2) K. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Structure solution and refinement were performed by using the SHELXL-97 package [41]. Crystal data collection and refinement details are given in Table 5.

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Appendix A. Supplementary material

CCDC 981405, contain the supplementary crystallographic data for **$Zn_3(L3)_6$** (**C3**). This data can be obtained free of charge via www.ccdc.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 email: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.03.013.

References

[1] G. Verdasco, M.A. Martin, B.de1. Castillo, P. Lopez-Alvarado, J.C. Menendez, Anal. Chim. Acta 303 (1995) 73–78.
[2] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515–1566.
[3] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, Nature 420 (2002) 759–760.
[4] W.M. Leevy, S.T. Gammon, H. Jiang, J.R. Johnson, D.J. Maxwell, E.N. Jackson, M. Marquez, D. Piwnica-Worms, B.D. Smith, J. Am. Chem. Soc. 128 (2006) 16476–16477.
[5] A.O. Eseola, W. Li, R. Gao, M. Zhang, X. Hao, T. Liang, N.O. Obi-Egbedi, W.-H. Sun, Inorg. Chem. 48 (2009) 9133–9146.
[6] Z. Tian, W. Wu, W. Wan, A.D.Q. Li, J. Am. Chem. Soc. 133 (2011) 16092–16100.
[7] C.W. Tang, S.A. VanSlyke, Appl. Phys. Lett. 51 (1987) 913–915.
[8] L.S. Sapochak, A. Padmaperuma, N. Washton, F. Endrino, G.T. Schmett, J. Marshall, D. Fogarty, P.E. Burrows, S.R. Forrest, J. Am. Chem. Soc. 123 (2001) 6300–6307.
[9] F.O. Suliman, S.N. Al-Busafi, M. Al-Risi, K.N. Al-Badi, Dyes Pigm. 92 (2012) 1153–1159.
[10] C. Perez-Bolivar, S.Y. Takizawa, G. Nishimura, V.A. Montes, P. Anzenbacher, Chem – A Eur. J. 17 (2011) 9076–9082.
[11] Y.-W. Shi, M.-M. Shi, J.-C. Huang, H.-Z. Chen, M. Wang, X.-D. Liu, Y.-G. Ma, H. Xu, B. Yang, Chem. Commun. (2006) 1941–1943.
[12] S.-H. Liao, J.-R. Shiu, S.-W. Liu, S.-J. Yeh, Y.-H. Chen, C.-T. Chen, T.J. Chow, C.-I. Wu, J. Am. Chem. Soc. 131 (2009) 763–777.
[13] C.H. Chen, J. Shi, Coord. Chem. Rev. 171 (1998) 161–174.
[14] M.D. Halls, H.B. Schlegel, Chem. Mater. 13 (2001) 2632–2640.
[15] S. Perumal, B. Minaev, H. Agren, J. Phys. Chem. C 117 (2013) 3446–3455.
[16] H.-P. Zeng, G.-R. Wang, G.-C. Zeng, J. Li, Dyes Pigm. 83 (2009) 155–161.
[17] C.J. Fahrni, T.V. O'Halloran, J. Am. Chem. Soc. 121 (1999) 11448–11458.
[18] M. Royzen, A. Durandin, V.G. Young Jr., N.E. Geacintov, J.W. Canary, J. Am. Chem. Soc. 128 (2006) 3854–3855.
[19] C. Zhang, Y. Zhang, Y. Chen, Z. Xie, Z. Liu, X. Dong, W. He, C. Shen, Z. Guo, Inorg. Chem. Commun. 14 (2011) 304–307.
[20] H.-H. Wang, Q. Gan, X.-J. Wang, L. Xue, S.-H. Liu, H. Jiang, Org. Lett. 9 (2007) 4995–4998.
[21] M.L. Ramos, A.R.E. De Sousa, L.L.G. Justino, S.M. Fonseca, C.F.G.C. Geraldes, H.D. Burrows, Dalton Trans. 42 (2013) 3682–3694.
[22] P.E. Burrow, L.S. Sapochak, D.M. McCarty, S.R. Forrest, M.E. Thompson, Appl. Phys. Lett. 64 (1994) 2718–2720.
[23] L.M.A. Monzon, F. Burke, J.M.D. Coey, J. Phys. Chem. C 115 (2011) 9182–9192.
[24] M. Brinkmann, B. Fite, S. Pratontep, C. Chaumont, Chem. Mater. 16 (2004) 4627–4633.
[25] A. Elschner, H.W. Heuer, F. Jonas, S. Kirchmeyer, R. Wehrmann, K. Wussow, Adv. Mater. 13 (2001) 1811–1814.
[26] R. Pohl, P. Anzenbacher Jr., Org. Lett. 5 (2003) 2769–2772.
[27] R. Pohl, V.A. Montes, J. Shinar, P. Anzenbacher Jr., J. Org. Chem. 69 (2004) 1723–1725.
[28] B.D. Muegge, S. Brooks, M.M. Richter, Anal. Chem. 75 (2003) 1102–1105.
[29] C. Pérez-Bolívar, L. Llovera, S.E. Lopez, P. Anzenbacher Jr., J. Lumin. 130 (2010) 145–152.
[30] F.O. Suliman, I. Al-Nafai, S.N. Al-Busafi, Spectrochim. Acta Part A: Mol. Biomol. Spectr. 118 (2014) 66–72.
[31] H. Jang, L.-M. Do, Y. Kim, J.G. Kim, T. Zyung, Y. Do, Synth. Met. 121 (2001) 1669–1670.
[32] A.O. Eseola, W. Li, W.-H. Sun, M. Zhang, L.W. Xiao, J.A.O. Woods, Dyes Pigm. 88 (2011) 262–273.
[33] Z. Zhou, W. Li, X. Hou, L. Chen, X. Hao, C. Redshaw, W.-H. Sun, Inorg. Chim. Acta 392 (2012) 292–299.
[34] Z. Zhou, W. Li, X. Hao, C. Redshaw, L.-Q. Chen, W.-H. Sun, Inorg. Chim. Acta 392 (2012) 345–353.
[35] J. Xia, Z. Zhou, W. Li, H.-Q. Zhang, C. Redshaw, W.-H. Sun, Inorg. Chim. Acta 394 (2013) 569–575.
[36] L. Li, X. Zhang, W. Zhang, W. Li, W.-H. Sun, C. Redshaw, Spectrochim. Acta Part A: Mol. Biomol. Spectr. 118 (2014) 1047–1055.
[37] G.R. Clemo, R. Howe, 5-Formyl-8-hydroxy-quinoline, J. Am. Chem. Soc. (1955) 3552–3553.
[38] P.C. Tway, L.J.C. Love, J. Phys. Chem. 86 (1982) 5223–5226.
[39] T. Qiu, X. Xu, X. Qian, J. Photochem. Photobiol. A 214 (2010) 86–91.
[40] A.V. Deshpande, U. Kumar, J. Fluoresc. 16 (2006) 679–687.
[41] G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.