Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 98 (2012) 396–404

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, spectroscopic characterization and crystal structure of novel NNNN-donor μ-bis(bidentate) tetraaza acyclic Schiff base ligands

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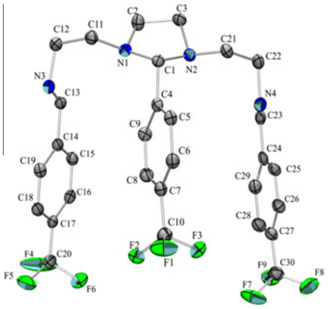
HIGHLIGHTS

- ▶ Three new tetraaza acyclic Schiff bases were prepared.
- ▶ Spectroscopic characterization and crystal structure were determined.
- ▶ Five-membered ring spacer as a novel type of imidazolidine ligand is formed.
- ▶ A novel spacer-cumbridging unit is formed.

GRAPHICAL ABSTRACT

Three new tetraaza N_4 acyclic Schiff bases with three pendant arms are prepared. The X-ray structure (TTFMB and TTDMB), UV–Vis, CV, FT-IR and MS of the Schiff bases have been determined.



ARTICLE INFO

Article history:
Received 5 July 2012
Received in revised form 10 August 2012
Accepted 21 August 2012
Available online 1 September 2012

Keywords:
Tetraaza acyclic
Imidazolidine ring
4-Substituted benzaldehydes
Pendant arms
Crystal structure

ABSTRACT

Novel NNNN-donor μ-bis(bidentate) tetraaza acyclic Schiff base ligands with different substituents (CF_3, $N(CH_3)_2$ or OH groups) were synthesized by the condensation reaction of triethylenetetramine with 4-substituted benzaldehydes. Triethylenetetramine tris(4-trifluoromethylbenzylidene) (TTFMB), triethylenetetramine tris(4-dimethylaminobenzylidene) (TTDMB) and triethylenetetramine tris(2,4-dihydroxybenzylidene) (TTDHB) were formed as N_4 donor ligands. The formation of a five-membered imidazolidine ring from the ethylenediamine backbone as a spacer-cumbridging unit gives rise to a new type of imidazolidine ligand. The structure of the TTFMB and TTDMB were determined by single crystal X-ray crystallography. The synthesized ligands have been characterized on the basis of the results of cyclic voltammetry (CV) and spectroscopic studies viz. FT-IR spectroscopy (FT-IR), mass spectroscopy (MS) and UV–Vis spectroscopy (UV–Vis).

Introduction

Schiff bases ligands with multidentate N donors have received sporadic attention for many year, but tetraaza acyclic ligands are still rare [1–3]. Schiff bases have been studied extensively since it is recognized that many complexes of this type with N_xO_y donor sets may serve as models for biologically important metal-containing species [4,5]. In studies of Schiff bases, the emphasis has been mainly on macrocyclic ligands, macrocycles with one open side, or polypodal ligands [6–8]. Among various products from the condensation of aromatic aldehydes with tetramine containing both primary and secondary amino groups is a binucleating Schiff base with an in-built spacer imidazolidine ring, which can take up two same or different metal ions [9–11]. The use of multidentate ligands has been receiving considerable attention in recent years following the identification of similar catalytically active biosites in living systems [12–14]. Recently we reported X-ray structural

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http://dx.doi.org/10.1016/j.saa.2012.08.064

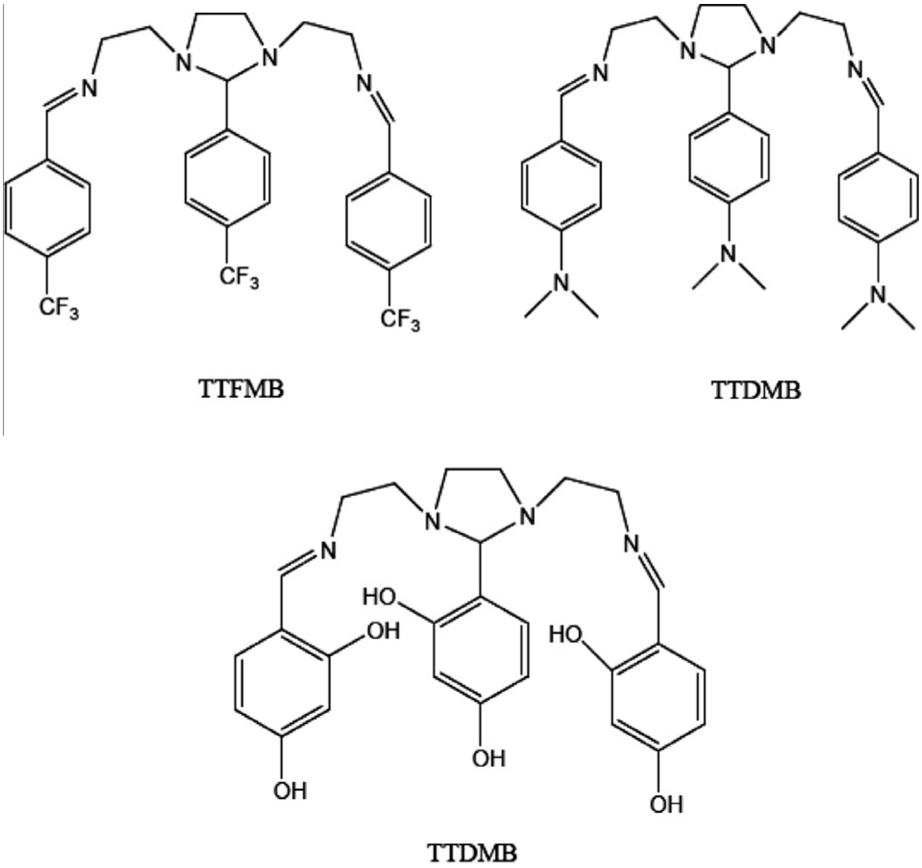

Fig. 1. Structure of the three new tetraaza acyclic ligands TTDMB, TTFMB and TTDHMB.

Table 1
Crystal data and structure refinement for TTDMB and TTFMB.

Chemical formula	$C_{33}H_{45}N_7$, TTDMB	$C_{30}H_{27}F_9N_4$, TTFMB
Formula weight	539.76	614.56
Temperature (K)	150(2)	150(2)
Radiation, wavelength (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, *Pc*
a (Å)	9.9799(13)	5.7301(5)
b (Å)	30.568(3)	10.9123(9)
c (Å)	19.951(3)	22.7746(18)
α (°)	90	90
β (°)	92.888	90.157
γ (°)	90	90
V (Å^3)	6078.7(13)	1424.1(2)
Z	8	2
Dcalc (g cm^{-3})	1.180	1.433
Crystal colour and size (mm)	Colourless, 0.19 ∗ 0.08 ∗ 0.08	Colourless, 0.64 ∗ 0.11 ∗ 0.06
μ (mm^{-1})	0.072	0.127
F(000)	2336	632
θ Range	2.7–20.1	2.6–23.0
Index ranges	$-9 < h < 9$, $-28 < k < 28$, $-18 < l < 18$	$-6 < h < 6$, $-12 < k < 12$, $-25 < l < 25$
Reflections collected	17925	18164
Independent reflections [Rint]	5358[0.0569]	2066[0.0447]
Reflections with $F^2 > 2\sigma$	3553	1975
Absorption correction	Numerical	Numerical
Maximum and minimum transmission	0.9867 and 0.9943	0.9235 and 0.9919
Data/restraints/parameters	5358/0/734	2066/2/390
Goodness-of-fit on F^2	0.995	1.064
Final *R* indices [$F^2 > 2\sigma$]	$R1 = 0.0433$, $wR2 = 0.0921$	$R1 = 0.0345$, $wR2 = 0.0859$
R indices (all data)	R1 = 0.0828, wR2 = 0.1079	$R1 = 0.0370$, $wR2 = 0.0884$
Largest difference peak, hole (eÅ^{-3})	0.15, 0.15	0.27, 0.20

characterization of one tetramine held by an imidazolidine ring [15]. In order to broaden our perspective on potentially tetraaza acyclic ligands, we have prepared the new tetraaza acyclic Schiff bases shown in Fig. 1. These ligands potentially act as tetradentate (NNNN) ligand but may act as bidentate ligands [16,17]. When the polyamines contain both primary and secondary amino groups,

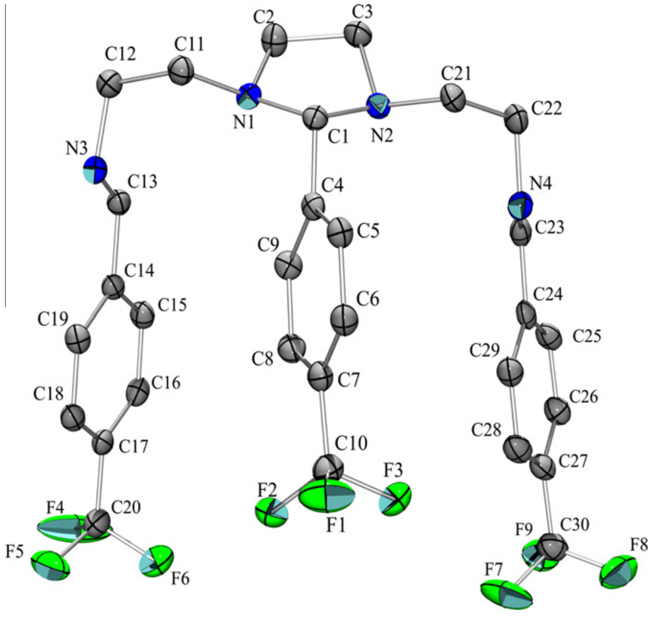

Fig. 2. ORTEP drawing of TTFMB ligand, 2-(4′-trifluoromethylphenyl)-l,3-bis[3′-aza-4′-(4″-trifluoromethylphenyl)-prop-4′-en-1′-yl]-1,3-imidazolinelne showing 50% probability displacement ellipsoids and the atom-numbering scheme.

either Schiff bases, imidazolines or Schiff bases containing additional imidazoline rings are obtained [18,19]. To study the effects of various substituent of imidazolines ring as pendant arms and spacer on structure and physico-chemical properties of the multidentate ligands, derivatives of benzaldehyde with CF_3, $N(CH_3)_2$ or OH groups were used in the synthesis of three new tetraaza acyclic Schiff bases. The relationship between the electronic properties and reactivity of these novel N_4-donor μ-bis(bidentate) tetraaza acyclic Schiff base ligands mimic some naturally occurring acyclic compounds [20,21]. These properties continue to endorse great interest in their design and preparation. Among the ligands employed for drug design, imidazolidine nucleus serves as an important pharmacophore in drug discovery [22,23]. Imidazolidines are very useful subunits for the development of molecules of pharmaceutical or biological interest. There are reports on tetraaza Schiff base ligands [11,16]. To the best of our knowledge there is no report on NNNN-donor μ-bis(bidentate) tetraaza acyclic Schiff base ligands with CF_3, $N(CH_3)_2$ or OH groups substituents. Considering all these specifics, spectroscopic properties and electrochemical activity of N_4-donor μ-bis(bidentate) tetraaza acyclic Schiff base ligands, with interesting physical and spectroscopic properties, have become our main significance.

In view of the above biological consequence and in continuation of our previous work [24–26], we here demonstrate a new strategy to introduce imidazolidine rings as subunits in tetraaza acyclic ligands employing novel precursors. The synthesis, spectroscopic studies, crystal structure and electrochemical properties of three new tetraaza acyclic Schiff bases with imidazolidine ring, spacer and two pendant arms from condensation of substituted benzaldehydes and triethylenetetramine (trien) are reported. The structures

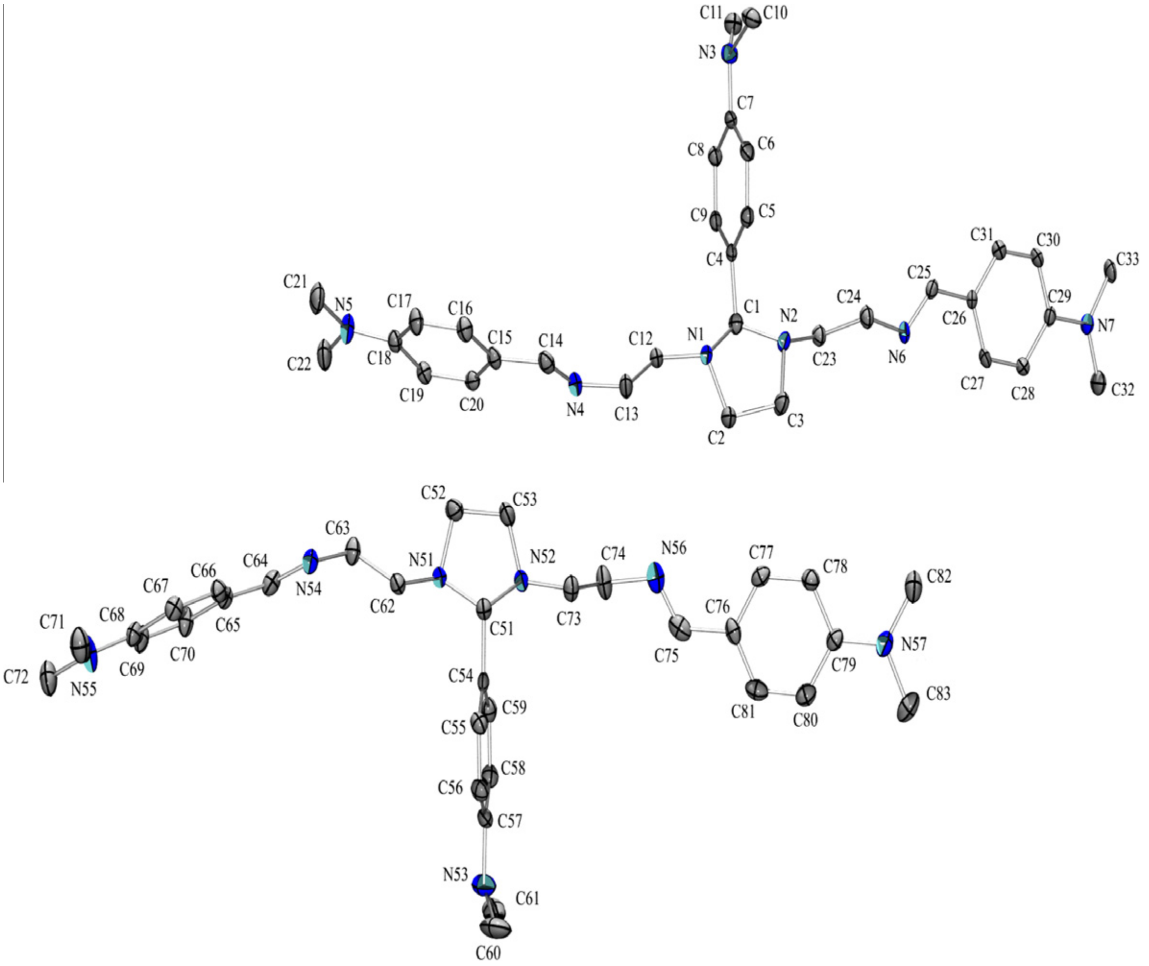

Fig. 3. ORTEP drawing of TTDMB ligand, 2-(4′-dimethylaminophenyl)-l,3-bis[3′-aza-4′-(4″-dimethylaminophenyl)-prop-4′-en-1′-yl]-1,3-imidazolinelne showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Table 2
Selected bond lengths (Å) for $C_{33}H_{45}N_7$ and $C_{30}H_{27}F_9N_4$.

Ligand	$C_{33}H_{45}N_7$		$C_{30}H_{27}F_9N_4$
Bond lengths			
N(1)–C(1)	1.472(4)	N(1)–C(1)	1.466(6)
N(1)–C(2)	1.462(4)	N(1)–C(2)	1.478(6)
N(1)–C(12)	1.457(4)	N(1)–C(11)	1.447(6)
N(2)–C(1)	1.463(4)	N(2)–C(1)	1.455(6)
N(2)–C(3)	1.468(4)	N(2)–C(3)	1.480(6)
N(2)–C(23)	1.449(4)	N(2)–C(21)	1.464(6)
N(3)–C(7)	1.394(4)	N(3)–C(12)	1.453(6)
N(3)–C(10)	1.455(4)	N(3)–C(13)	1.264(6)
N(3)–C(11)	1.457(4)	N(4)–C(22)	1.462(7)
N(4)–C(13)	1.466(4)	N(4)–C(23)	1.259(7)
N(4)–C(14)	1.266(4)		
N(5)–C(18)	1.382(4)		
N(5)–C(21)	1.447(5)		
N(5)–C(22)	1.436(5)		
N(6)–C(24)	1.455(4)		
N(6)–C(25)	1.271(4)		
N(7)–C(29)	1.375(4)		
N(7)–C(32)	1.433(4)		
N(7)–C(33)	1.450(4)		
N(51)–C(51)	1.486(4)		
N(51)–C(52)	1.467(4)		
N(51)–C(62)	1.453(4)		
N(52)–C(51)	1.448(4)		
N(52)–C(53)	1.457(4)		
N(52)–C(73)	1.458(4)		
N(53)–C(57)	1.399(5)		
N(53)–C(60)	1.444(5)		
N(53)–C(61)	1.446(5)		
N(54)–C(63)	1.465(4)		
N(54)–C(64)	1.268(4)		
N(55)–C(68)	1.381(4)		
N(55)–C(71)	1.430(5)		
N(55)–C(72)	1.435(5)		
N(56)–C(74)	1.480(5)		
N(56)–C(75)	1.246(5)		
N(57)–C(79)	1.372(4)		
N(57)–C(82)	1.436(5)		
N(57)–C(83)	1.457(5)		

Table 3
Selected bond angle (°) for $C_{33}H_{45}N_7$ and $C_{30}H_{27}F_9N_4$.

Bond angles	$C_{33}H_{45}N_7$		$C_{30}H_{27}F_9N_4$
C(1)–N(1)–C(2)	103.1(3)	C(1)–N(1)–C(2)	108.1(3)
C(1)–N(1)–C(12)	112.5(3)	C(1)–N(1)–C(11)	114.3(3)
C(2)–N(1)–C(12)	113.5(3)	C(2)–N(1)–C(11)	115.2(4)
C(1)–N(2)–C(3)	108.0(2)	C(1)–N(2)–C(3)	105.0(3)
C(1)–N(2)–C(23)	114.9(3)	C(1)–N(2)–C(21)	112.5(3)
C(3)–N(2)–C(23)	116.0(3)	C(3)–N(2)–C(21)	112.8(4)
C(7)–N(3)–C(10)	117.9(3)	C(12)–N(3)–C(13)	116.4(4)
C(7)–N(3)–C(11)	118.5(3)	C(22)–N(4)–C(23)	118.8(4)
C(10)–N(3)–C(11)	114.3(3)		
C(13)–N(4)–C(14)	115.8(4)		
C(18)–N(5)–C(21)	119.5(3)		
C(18)–N(5)–C(22)	121.7(3)		
C(21)–N(5)–C(22)	117.8(3)		
C(24)–N(6)–C(25)	118.5(3)		
C(29)–N(7)–C(32)	120.6(3)		
C(29)–N(7)–C(33)	119.8(3)		
C(32)–N(7)–C(33)	118.7(3)		
C(51)–N(51)–C(52)	104.0(3)		
C(51)–N(51)–C(62)	111.9(3)		
C(52)–N(51)–C(62)	113.2(3)		
C(51)–N(52)–C(53)	108.0(3)		
C(51)–N(52)–C(73)	115.1(3)		
C(53)–N(52)–C(73)	114.9(3)		
C(57)–N(53)–C(60)	118.1(4)		
C(57)–N(53)–C(61)	120.8(4)		
C(60)–N(53)–C(61)	114.8(4)		
C(63)–N(54)–C(64)	117.1(3)		
C(68)–N(55)–C(71)	121.1(3)		
C(68)–N(55)–C(72)	120.7(4)		
C(71)–N(55)–C(72)	118.0(3)		
C(74)–N(56)–C(75)	116.0(4)		
C(79)–N(57)–C(82)	120.4(3)		
C(79)–N(57)–C(83)	120.1(4)		
C(82)–N(57)–C(83)	118.8(3)		

of TTTFMB and TTDMB were characterized using single crystal X-ray crystallography. UV–Vis, FT-IR, mass spectroscopy and electrochemical properties of the TTFMB, TTDHB and TTDMB (Fig. 1) were studied.

Experimental

Materials and methods

Triethylenetetramine hydrate (trien), 4-dimethylaminobenzaldehyde, 4-trifluoromethyl-benzaldehyde and 2,4-dihydroxybenzaldehyde, were purchased from Aldrich or Alfa and were used without further purification. Infrared spectra were recorded as KBr disks in the range 4000–400 cm^{-1} on a Bruker FT-IR (Tensor 27) spectrophotometer. Mass spectra were obtained with Platform II from Micromass. UV/Vis spectra were recorded on a Varian Cary 500 Scan spectrophotometer. Cyclic voltammograms (CV) were recorded by using a SAMA Research Analyzer M-500. Three electrodes were utilized in this system, a glassy carbon working electrode, a platinum disk auxiliary electrode and Ag/Ag$^+$ as reference electrode. The glassy carbon working electrode (Metrohm 6.1204.110) with 2.0 ± 0.1 mm diameter was manually cleaned with 1 lm alumina polish prior to each scan. Tetrabutylammonium tetrafluoroborate (n-Bu)$_4$NBF$_4$, was used as supporting electrolyte. All electrochemical potentials were calibrated vs. internal Fc$^{+/o}$ (E^0 = 0.40 V vs. SCE) couple under the same conditions.

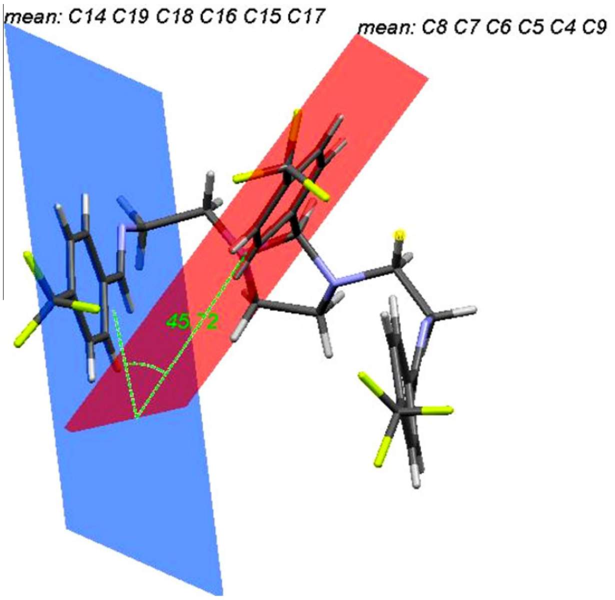

Fig. 4. Dihedral angle of TTFMB showing 45.72° angles between pendant arms and the spacer.

Single crystals suitable for X-ray diffraction were obtained as described in the Experimental Section. Single crystals of TTFMB and TTDMB were mounted on a MiTeGen mout with Paratone oil and cooled to −150 °C in a stream of nitrogen gas. Data collection were performed on a Bruker Kappa APEXII DUO diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were integrated using SAINT [27] software and absorption corrections were applied using program SADABS [28]. The structures were solved by direct methods and refined by full-matrix least-

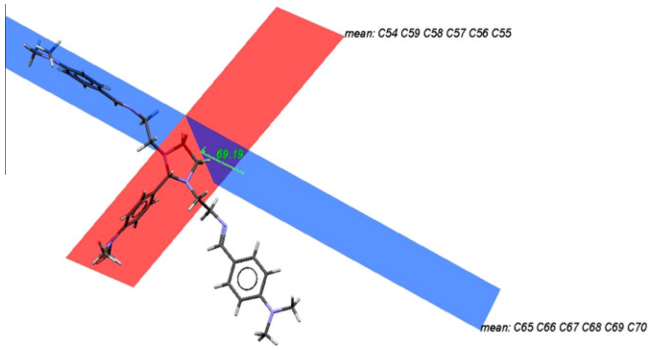

Fig. 5. Dihedral angle of TTDMB showing 69.19° angles between pendant arms and the spacer.

squares using SHELTXL [29]. Experimental and refinement parameters are summarized in Table 1. In both cases diffraction was weak and required long exposure times to measure the data; for TTFMB data were recorded to a resolution of 0.9 Å and for TTDMB to 1 Å. In TTFMB, Friedel pairs were merged during final refinement, due to lack of significant anomalous dispersion data. Probable disorder of fluorine atoms in TTFMB was not modeled, in order to support the poor data-to-paramater ratio. TTFMB was refined as a pseudo-merohedral twin, with twin law 100/0−10/00−1 and an 18.38(18)% contribution from the minor twin component.

Synthesis

In a one-pot reaction the ligand was prepared by the condensation of 1 equivalent of trien and 3 equivalents of 4-substituted benzaldehyde (Fig. 1). The desired 4-substituted benzylidene was synthesized as described in the experimental section and gave a good overall yield for one pot synthesis of 72–90%. Starting from the 4-substituted benzaldehydes and triethylenetetramine (trien) the desired Schiff bases containing imidazolidine rings TTFMB, TTDMB and TTDHB were produced (Fig. 1). Final purification was achieved by recrystallization.

2-(4′-Dimethylaminophenyl)-l,3-bis[3′-aza-4′-(4″-dimethylamino-phenyl)-prop-4′-en-1′-yl]-1,3-imidazolinelne (TTDMB)

A solution of 0.75 mmol of trien in 2.5 mL of ethanol was added to a stirred solution of 3 mmol of 4-dimethylaminobenzaldehyde in 2.5 mL ethanol for 3 h at 30 °C. The product was filtered out, washed with cold ethanol and subsequently dried over anhydrous $CaCl_2$ in a desiccators yielding 75%, mp 167 °C. Recrystallization from ethanol afforded X-ray quality crystals. Mass spectrum (EI): 539 (M$^+$ = TTDMB$^+$). Infrared spectrum (cm^{-1}, KBr disk): 1638 (s, C=N), 1176 (s, C–N). UV–Vis (λ_{max}/nm): 270, 305.

2-(4′-Trifluoromethylphenyl)-l,3-bis[3′-aza-4′-(4″-trifluoromethyl-phenyl)-prop-4′-en-1′-yl]-1,3-imidazolinelne (TTFMB)

This was synthesized by the procedure outlined above for TTDMB using trien (0.75 mmol) and 4-trifluoromethylbenzaldehyde (3 mmol).

Recrystallization from ethanol afforded X-ray quality crystals. The yield was 72%; mp 110 °C. Mass spectrum (EI): 614 (M$^+$ - = TTFMB$^+$). Infrared spectrum (cm^{-1}, KBr disk): 1650 (s, C=N), 1328 (s, C–F). UV–Vis (λ_{max}/nm): 297.

2-(2′,4′-Dihydroxyphenyl)-l,3-bis[3′-aza-4′-(2″,4″-dihydroxy-phenyl)-prop-4′-en-1′-yl]-1,3-imidazolinelne (TTDHMB)

A solution of 0.75 mmol of trien in 2.5 mL of ethanol was added to a solution of 3 mmol of 2,4-dihydroxybenzaldehyde in 2.5 mL of

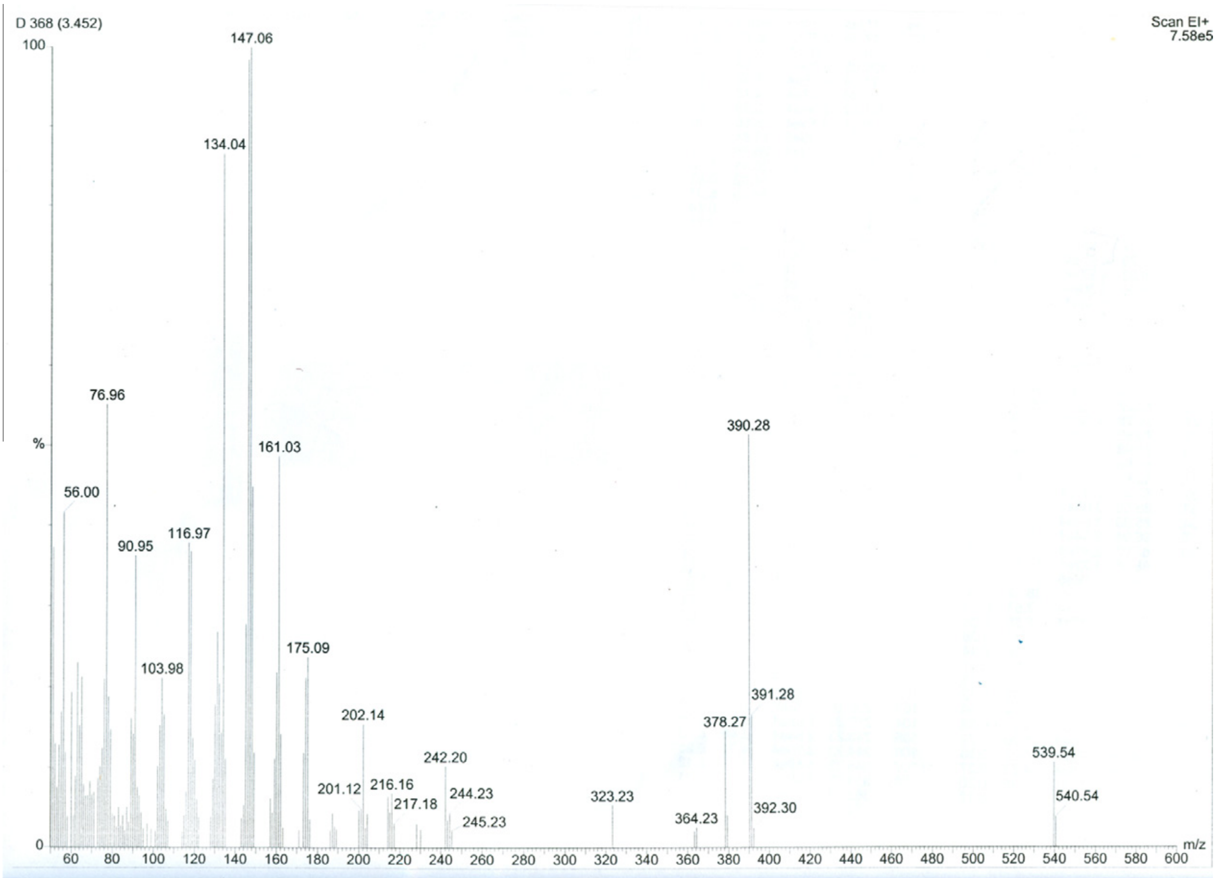

Fig. 6. Mass spectra of TTDMB ligand, 2-(4′-dimethylaminophenyl)-l,3-bis[3′-aza-4′-(4″-dimethylaminophenyl)-prop-4′-en-1′-yl]-1,3-imidazolinelne.

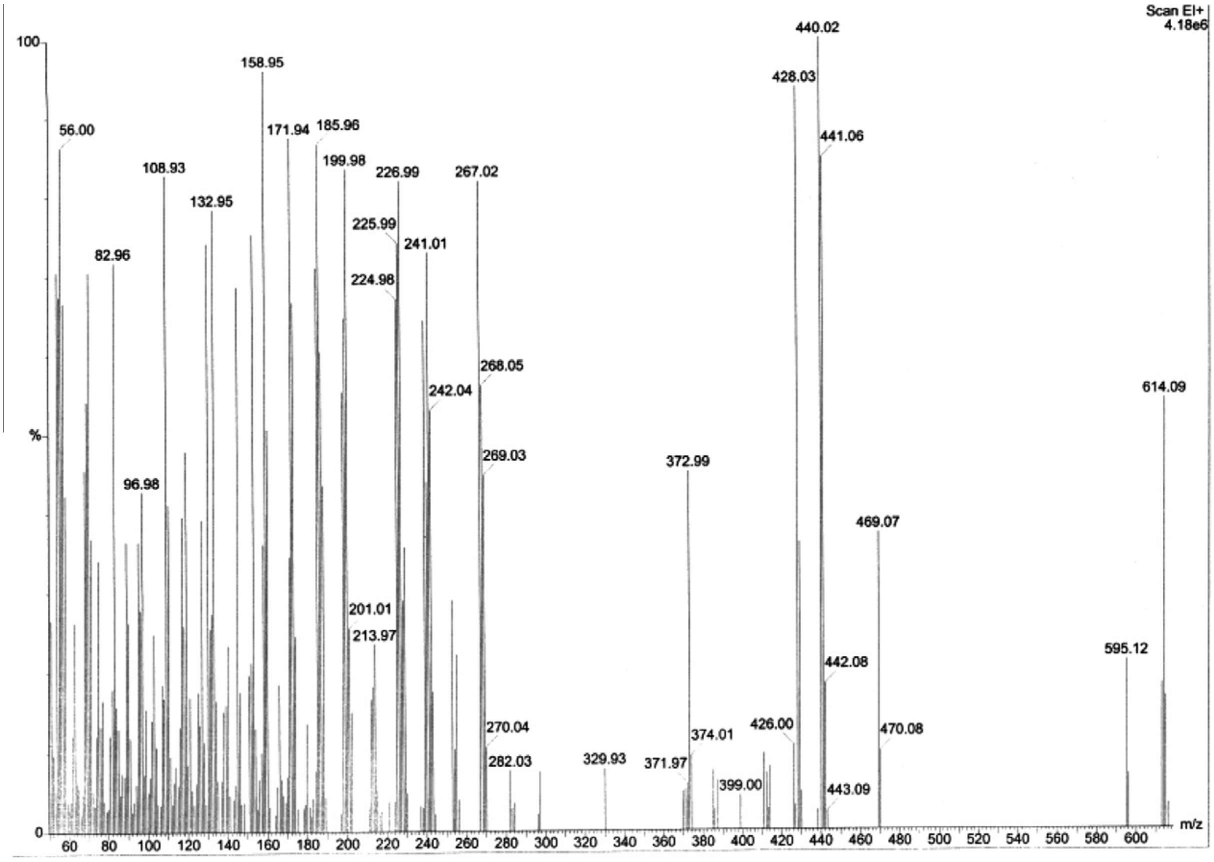

Fig. 7. Mass spectra of TTFMB ligand, 2-(4′-trifluoromethylphenyl)-l,3-bis[3′-aza-4′-(4″-trifluoromethylphenyl)-prop-4′-en-1′-yl]-1,3-imidazolinelne.

ethanol. An orange precipitate was formed in 7 days. The product was isolated by filtration, washed with cold ethanol and dried at room temperature for a yield of 90%, mp 300 °C. Mass spectrum (EI): 509 (M^+ = $TTDHMB^+$). Infrared spectrum (cm^{-1}, KBr disk): 1636 (s, C═N), 1360 (s, C–O), 3425 (m, O-H).UV–Vis (λ_{max}/nm): 280, 310, 380.

Electrochemical studies

The cyclic voltammograms of the three new tetraaza acyclic Schiff bases were conducted at 25 °C under an argon atmosphere using DMF solutions containing 0.05 mol dm^{-3}, $(n\text{-}Bu)_4NBF_4$ as supporting electrolyte and complex concentrations of about 3×10^{-3} mol dm^{-3}.

Results and discussion

Three new tetraaza acyclic Schiff bases TTFMB, TTDHB and TTDMB used in this work belongs to a new class of μ-bis(bidentate) type with substituted five-membered imidazolidine spacer. The synthesis and characterization of three tribenzylidinetriethylenetetramine ligands, TTFMB, TTDHB and TTDMB are described in this work. The ligand with bis imine groups separated by a flexible semi rigid imidazolidine ring can behave as a good bis(bidentate)-N,N donor. This type of ligands is also favourable for the formation of an infinite self-assembly which is not achieved with other ligand system [30].

X-ray diffraction studies

Crystals of TTTFMB ($C_{30}H_{27}F_9N_4$) are monoclinic, space group *Pc*, *a* = 5.7301(5) Å, *b* = 10.9123(9) Å, *c* = 22.7746(18) Å, *β* = 90.157(5)°, *Z* = 2; those of TTDMB ($C_{33}H_{45}N_7$) are monoclinic, $P2_1$/c, *a* = 9.9799(13) Å, *b* = 30.568(3) Å, *c* = 19.951(3) Å, *β* = 92.888(2)°, *Z* = 8. ORTEP views of the TTFMB and TTDHMB are shown in Figs. 2 and 3 respectively. Experimental details are reported in Table 1, selected bond lengths in Table 2 and bond angles in Table 3 The structure of TTDMB contains two crystallographically unique molecules in the asymmetric unit; molecule A (defined by atoms N1 to C33) and molecule B (defined by atoms N51 to C83. In both TTFMB and TTDMB, all of the angles and distances are in the range of those expected for this kind of Schiff base [31], and each adopts a conformation which is determined by the formation of a five-membered imidazolinic ring. The N3–C13 and N4–C23 distances of 1.264(6) Å and 1.259(9) Å in TTFMB, and N4–C14 [N54–C64] and N6–C25 [N56–C75] distances of 1.226(4) Å [1.268(4) Å] and 1.271(4) Å [1.246(5) Å] in TTDMB correspond to an N═C double bond. Figs. 4 and 5 show the dihedral angle of TTFMB and TTDMB with 45.72° and 69.19° angle between pendant arms and the spacer respectively. More electron withdrawing substituent, CF_3 of phenyl group will weaken the magnitude of electron density, at least around the nearest primary amine, thereby reducing the distances between pendant arms and the spacer while the mre electron donating substituent, $N(CH_3)_2$ of phenyl group will enhance the distances between pendant arms and the spacer.

Spectroscopic studies

Mass spectrometry

The electron impact mass spectrum of the three new tetraaza acyclic ligands confirms the proposed formula by showing peaks (*m*/*z*) at 539 (M^+ = $TTDMB^+$), 614 (M^+ = $TTFMB^+$), 509 (M^+ = $TTDHMB^+$) which indicates the formation of the desired imidazolidino N_4 Schiff base ligand. The EI mass spectrums of the

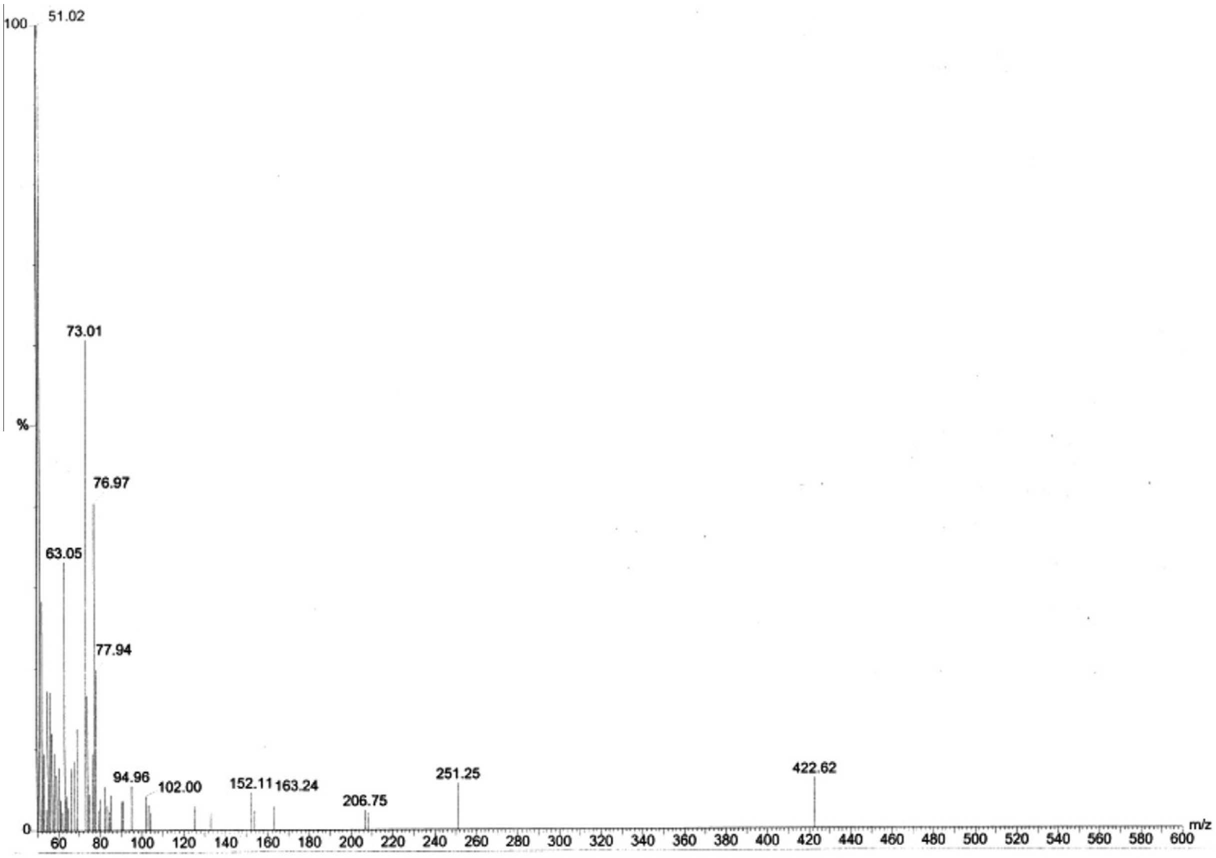

Fig. 8. Mass spectra of TTDHMB ligand, 2-(2′,4′-dihydroxyphenyl)-l,3-bis[3′-aza-4′-(2″,4″-dihydroxy-phenyl)-prop-4′-en-1′-yl]-1,3-imidazolinelne.

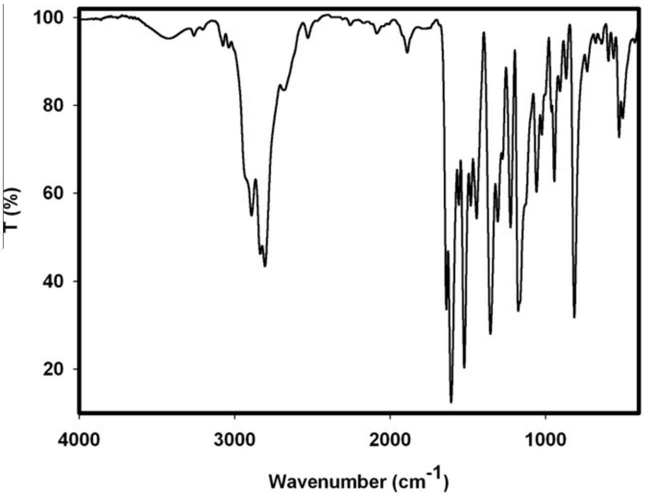

Fig. 9. FT-IR spectra of TTDMB ligand, 2-(4′-dimethylaminophenyl)-l,3-bis[3′-aza-4′-(4″-dimethylaminophenyl)-prop-4′-en-1′-yl]-1,3-imidazolinelne.

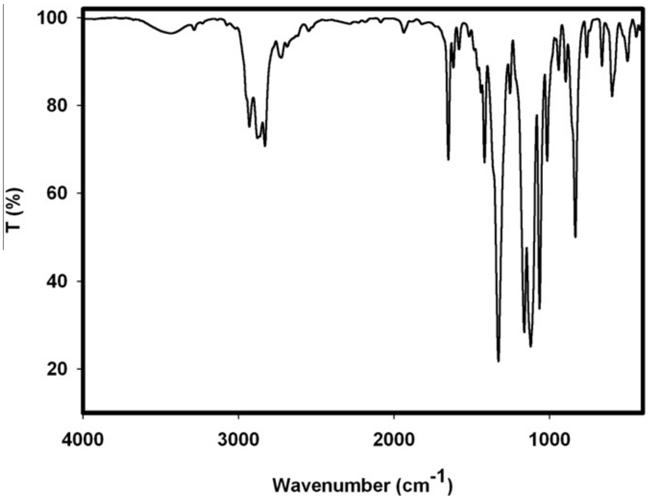

Fig. 10. FT-IR spectra of TTFMB ligand, 2-(4′-trifluoromethylphenyl)-l,3-bis[3′-aza-4′-(4″-trifluoromethylphenyl)-prop-4′-en-1′-yl]-1,3-imidazolinelne.

ligands are shown in Figs. 6–8 respectively. The molecular peaks of the cations are observed with the same isotopic distribution as the theoretical ones.

FT-IR spectra

IR spectra of the three new tetraaza acyclic ligands TTDMB, TTFMB and TTDHMB are shown in Fig. 9–11 respectively. IR spectra of the ligands show strong C═N stretching frequency of the imine functions at 1650 cm^{-1} (TTDMB), 1636 cm^{-1} (TTFMB), 1638 cm^{-1} (TTDHMB) which is shifted from the TTDMB, TTDHMB, TTFMB. In the IR spectrum of the ligands the absence of band in the region 3400 cm−1 (corresponding to free primary diamine) suggests that complete condensation of amino group with keto group [32]. Appearance of a new strong absorption band at 1639–1650 cm^{-1} range attributable to the characteristic stretching frequencies of the imino linkage υ(C═N). The absorption in IR spectrum of (L) in the range of 730–770 cm^{-1} is due to the presence of phenyl group. The electron withdrawing effect of substituent of phenyl group will

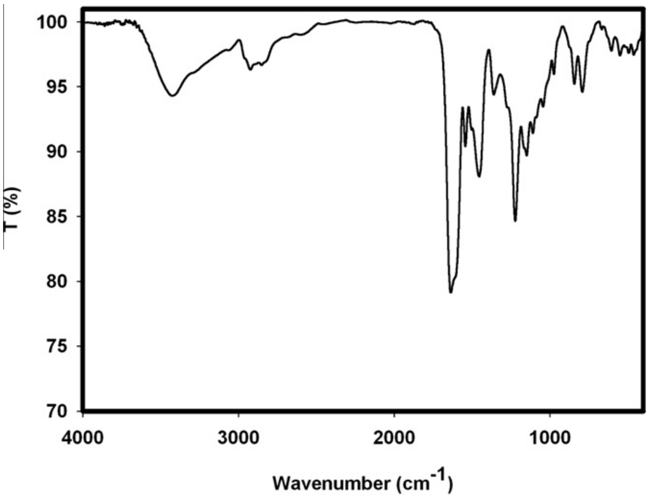

Fig. 11. FT-IR spectra of TTDHMB ligand, 2-(2′,4′-dihydroxyphenyl)-l,3-bis[3′-aza-4′-(2″,4″-dihydroxy-phenyl)-prop-4′-en-1′-yl]-1,3-imidazolinelne.

Table 4
Electronic spectral data of the three new tetraaza acyclic ligands TTDMB, TTFMB and TTDHMB in methanol.

TTDMB	TTFMB	TTDHMB
270 nm (π–π*) (920 M^{-1} cm^{-1}) 305 (n–π*)	297 nm (π–π*) (1533 M^{-1} cm^{-1})	280 nm (π–π*) (800 M^{-1} cm^{-1}) 310, 380 nm (n–π*)

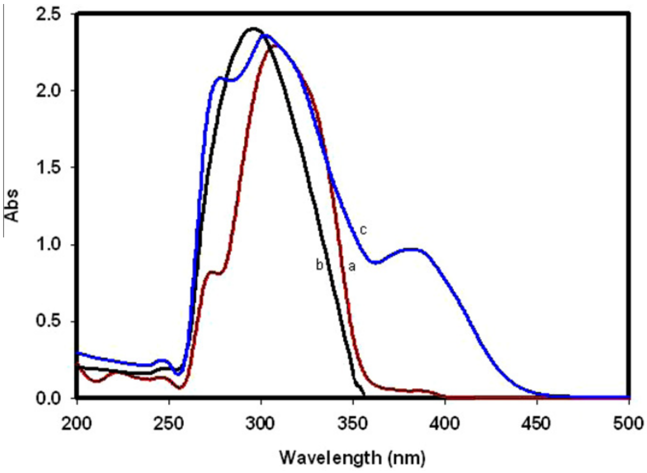

Fig. 12. UV–Vis of (a) TTDMB, (b) TTFMB and (c) TTDHMB ligands.

weaken the magnitude of electron density, at least around the nearest primary amine, thereby reducing the υC=N stretching frequency. The other effect of substituents is steric, as the rather bulky pendant group will hinder the movement of reactants into the site where reaction can take place. In models shown in Fig. 1, some conformations of the phenyl group lead to steric blocking being clearly significant. Both aspects are more severe at the primary amine closest to the phenyl group. X-ray crystal structure evidence, strongly support this argument.

Electronic spectra

Electronic spectra for TTDMB, TTFMB and TTDHMB were collected in methanol and molar absorptivity data are summarized in Table 4 Generally, two absorbance maxima were observed in

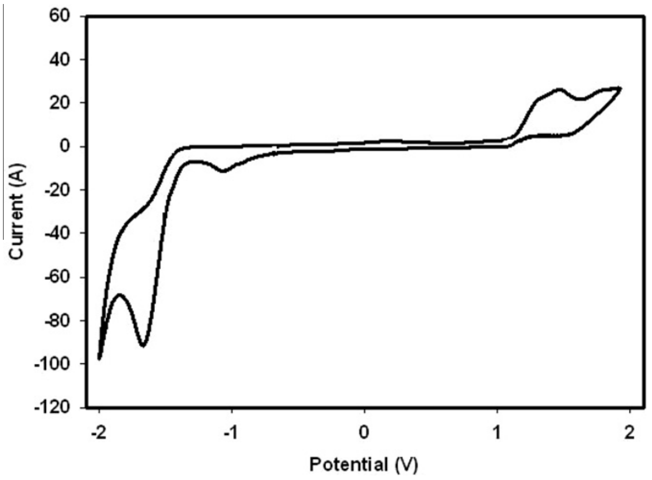

Fig. 13a. Cyclic voltammogram of TTDMB in DMF solution stored for 48 h at 293 K. Scan rate: 100 mV/s. $c = 3.0 \times 10^{-3}$.

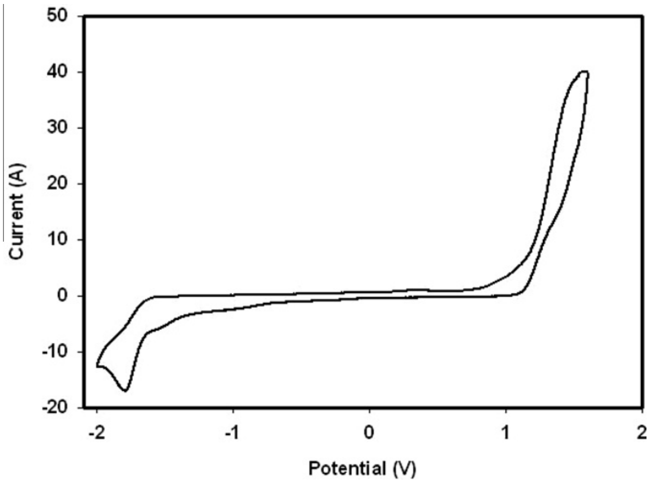

Fig. 13b. Cyclic voltammogram of TTFMB in DMF solution stored for 48 h at 293 K. Scan rate: 100 mV/s. $c = 3.0 \times 10^{-3}$.

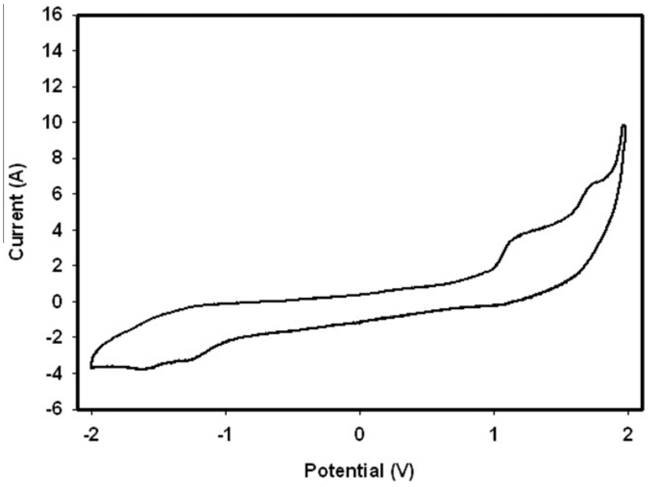

Fig. 13c. Cyclic voltammogram of TTDHMB in DMF solution stored for 48 h at 293 K. Scan rate: 100 mV/s. $c = 3.0 \times 10^{-3}$.

ranges of 270–297 nm and 305–380 nm. The electronic spectra of TTDMB in methanol have a maxima at 270 nm (Fig. 12) which can be related to the spin allowed π–π* azomethene intraligand transition [33]. The band at 305 nm can be assigned to spin-allowed n–π* transition. The absorbance spectra of ligands TTFMB and TTDHMB show maxima at 297 and 280 nm respectively which are proposed to be ligand based π–π* transitions.

Electrochemistry

The electrochemical behaviour of three new tetraaza acyclic ligands TTDMB, TTFMB and TTDHMB was investigated in dimethylformamide by cyclic voltammetry which are shown in Figs. 13a–c respectively. The voltammetric profile (Fig. 13a) for TTDMB on first scan displays one oxidation wave at 1.50 V while TTFMB (Fig. 13b) shows no electron transfer oxidation. The voltammetric profile (Fig. 13c) for TTDHMB shows two oxidation waves at 1.11, 1.78 V, which appears to be completely irreversible (i.e., these lack corresponding return waves), while a separate, irreversible reduction at −1.84, −1.91 and −1.50 V vs. SCE (again without its corresponding oxidation wave) is observed for one-electron transfer respectively. The lack of corresponding return waves is attributed to the large separation in ΔEp value.

Conclusion

Three new tetraaza acyclic Schiff bases TTFMB, TTDHB and TTDMB with imidazolidine ring have been prepared by the reaction of 4-substituted benzaldehydes and triethylenetetramine (trien) with imidazolidine ring. The effects of various substituents (CF_3, $N(CH_3)_2$ or OH groups) on structure and physico-chemical properties of the multidentate ligands were studied. The ligands with bis imine groups separated by a flexible semi rigid imidazolidine ring can behave as a good N_4 donor. The electron withdrawing effect of substituent of phenyl group will weaken the magnitude of electron density, at least around the nearest primary amine, thereby reducing the distances between pendant arms and the spacer while the electron donating $N(CH_3)_2$ of phenyl group will enhance the distances between pendant arms and the spacer. The novel NNNN-donor μ-bis(bidentate) tetraaza acyclic Schiff base ligands with different substituents (CF_3, $N(CH_3)_2$ or OH groups) exhibit absorbance maxima related to the intraligand transition. The electrochemical behaviour shows oxidation waves related to electron transfer reaction by cyclic voltammetry. Based on these results and straightforward synthesis, ligands are interesting candidates for mimic biological electron-transport.

Acknowledgements

The authors wish to thank the University of Isfahan for financially supporting this work. The diffractometer was purchased with funding from NSF Grant CHE-0741837.

Appendix A. Supplementary material

CCDC 826165 and 826166 contains the supplementary crystallographic data for ligand. 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.

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