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Synthesis, Structure and Photophysical Properties of a Highly Luminescent Terpyridine-Diphenylacetylene Hybrid Fluorophore and its Metal Complexes

Biswa Nath Ghosh, Filip Topić, Prasit Kumar Sahoo, Prasenjit Mal, Jarno Linnera, Elina Kalenius, Heikki M. Tuononen, and Kari Rissanen

A new fluorescent terpyridyl-diphenylacetylene hybrid fluorophore 4′-[4-[(4-methoxyphenyl)ethynyl]phenyl]-2,2′:6′,2″-terpyridine, L, was synthesized via Sonogashira cross-coupling of 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine and 4-ethynylanisole in the presence of Pd(PPh₃)₄/CuI as a catalyst. The solid state structure of L shows a trans arrangement of pyridine nitrogen atoms along the interannular bond in the terpyridine domain. Five transition metal complexes of L, [FeL₂](CF₃SO₃)₂ (1), [ZnL₂](ClO₄)₂ (2), [CdL₂](ClO₄)₂ (3), [RuL₂](PF₆)₂ (4), and PtMe₃IL (5), have also been synthesized and characterized by spectroscopic methods and single crystal X-ray analysis. The X-ray crystal structures of complexes 1-3 show a distorted octahedral MN₆ arrangement with tridentate coordination of the two terpyridine ligands, whereas in complex 5 the ligand L binds in bidentate fashion. The ligand L displays bright blue emission in the solid state and in both non-polar and polar organic media. The fluorescence quantum yield of L is exceptionally high for a monoterpyridine ligand of its kind, which can be rationalized with density functional theory calculations. The electronic structure of L shows that the fluorescence involves intramolecular charge transfer from the diphenylacetylene moiety to the terpyridine group, and it is not affected by the usual non-radiative relaxation processes such as pyridine rotation. The Fe(II), Ru(II) and Pt(IV) complexes of L were found to be non-emissive, whereas both Zn(II) and Cd(II) complexes displayed significant green emission attributed to intra-ligand charge transfer states. These results were supported by the observed red-shift of the emission maxima of complexes 2 and 3 upon increasing the solvent polarity.

Introduction

The well-known 2,2′:6′,2″-terpyridine and its derivatives represent an important class of ligands in the fields of supramolecular and coordination chemistry as well as material science.1 Their strong chelating properties, stemming from the arrangement of the three pyridinic nitrogen atoms, along with the extremely strong binding affinity towards most transition metal ions make terpyridines highly useful building blocks for the creation of wide range of systems with interesting photophysical, electrochemical, and catalytic properties.2 Consequently, 2,2′:6′,2″-terpyridine and its transition metal complexes have been explored extensively for use in dye-sensitized solar cells,3 two-photon luminescent systems,4 mixed-valence chemistry,5 as well as electrochromic6 and organic light-emitting devices.7 In addition, terpyridines have often been used in the construction of self-assembled hydrogels8 with myriad applications in organic-inorganic hybrid materials, medicines, and optoelectronics.9

Fluorescence response from metallo-terpyridine complexes, especially those with Zn10, has recently prompted the development of new sensors for bio-assays and in vivo imaging purposes.10 It is unfortunate that many terpyridine derivatives have low quantum yields due to efficient non-radiative relaxation processes, and any significant emission can only be achieved after specific modifications to the terpyridine backbone.11 For this reason, considerable research effort has been invested in examining the structure-function relationships in terpyridines to intelligently tune their luminescence properties. It has been established that the emission of 2,2′:6′,2″-terpyridines can be greatly influenced by introducing a conjugated moiety at the 4″ position.12 In this context, it is somewhat surprising that there exist only very few structural reports of 4″ substituted terpyridine derivatives with 1,2-diphenylacetylene (tolan), one of the archetypical organic fluorophores.13 To the best of our knowledge, the crystal structure of a Fe₂(CO)₉(μ-azadiethiolate) cluster bearing a pendant terpyridine domain with an alkynylphenylene spacer represents the only structurally characterized example in the literature,14 but the authors did not study its fluorescence properties.

Herein, we report the synthesis and crystal structure of a new monoterpyridine ligand L, 4′-[4-[(4-methoxyphenyl)ethynyl]phenyl]-2,2′:6′,2″-terpyridine, which merges the diphenylacetylene moiety with the terpyridine framework and shows strong blue fluorescence both in solution and in the solid state. The syntheses and crystal structures of several transition metal complexes of L are also described,
Synthesis of [FeL2](CF3SO3)2 (1). To a degassed acetonitrile solution (10 mL) of Fe(CF3SO3)2 (20 mg, 0.057 mmol), 50.0 mg (0.114 mmol) of ligand L was added and the reaction mixture was stirred at room temperature for 1 h. The mixture was then concentrated after which an excess of diethyl ether (30 mL) was added slowly. The resultant purple solid, I, was filtered, washed with diethyl ether, and dried under vacuum. Yield 86% (60 mg). The salt I was crystallized as purple crystals upon slow diffusion of disopropyl ether into its acetonitrile solution at room temperature.

1H NMR (400 MHz, CD3CN, 27 °C) δ/ppm: 9.21 (s, 4H), 8.63 (d, 4H, J 7.9 Hz), 8.36 (dt, 4H, J 1.8, 8.4 Hz), 7.89-7.95 (m, 8H), 7.59 (dt, 4H, J 2.0, 8.8 Hz), 7.20 (d, 4H, J 5.6 Hz), 7.09 (td, 4H, J 1.2, 6.8 Hz), 7.03 (dt, 4H, J 2.0, 8.8 Hz), 3.87 (s, 6H). MS (ESI-TOF) [FeL2]+ m/z 467.1353 (Calcd. 467.1354), [FeL2+CF3SO3]+ m/z 503.1229 (Calcd. 503.1228). Anal. Calcd. for CdH6FeN2O6S: 1233.00%: C, 60.39; H, 3.43; N, 6.82. Found: C, 60.12; H, 3.62; N, 6.72%.

Synthesis of [ZnL2](ClO4)2 (2). To an acetonitrile solution (10 mL) of Zn(ClO4)2·6H2O (20 mg, 0.054 mmol), 47.2 mg (0.107 mmol) of ligand L in 10 mL dichloromethane was added and the reaction mixture was stirred at room temperature for 2 h. The resultant mixture was then concentrated and evaporated to dryness to afford a greenish-yellow product. The product was re-dissolved in a minimal volume of acetonitrile and excess of diethyl ether (25 mL) was added to precipitate 2. The precipitate was filtered, washed again several times with diethyl ether, and dried in vacuum. Yield 81% (50 mg). Slow diffusion of disopropyl ether into a 2:1 mixture of acetonitrile and dichloromethane at room temperature afforded yellow crystals.

1H NMR (400 MHz, CD3CN, 27 °C) δ/ppm: 8.99 (s, 4H), 8.72 (d, 4H, J 8.1 Hz), 8.15-8.24 (m, 4H), 7.88 (d, 4H, J 8.4 Hz), 7.84 (d, 4H, J 4.5 Hz), 7.57 (dt, 4H, J 1.8, 8.8 Hz), 7.41 (dd, 4H, J 1.5, 5.9 Hz), 7.02 (d, 4H, J 8.9 Hz), 3.86 (s, 6H). MS (ESI-TOF) [ZnL2]+ m/z 471.1346 (Calcd. 471.1325), [ZnL2+ClO4]+ m/z 504.1322 (Calcd. 504.1217). Anal. Calcd. for CdH6Cl2N2O6Zn (1143.30): C, 63.03; H, 3.70; N, 7.35. Found: C, 63.39; H, 3.93; N, 7.02%.

Synthesis of [CdL2](ClO4)2 (3). To an acetonitrile solution (10 mL) of Cd(ClO4)2·6H2O (24.2 mg, 0.058 mmol), 51.8 mg (0.118 mmol) of ligand L in 10 mL dichloromethane was added and the reaction mixture was stirred at room temperature for 3 h. The resultant mixture was then concentrated and evaporated to dryness. The product was re-dissolved in a minimal volume of acetonitrile and excess of diethyl ether (25 mL) was added to precipitate a yellow product. The precipitate was filtered, washed again several times with diethyl ether, and dried in vacuum. Yield 79% (54 mg). The product was crystallized upon slow diffusion of disopropyl ether into its acetonitrile solution at room temperature. 1H NMR (400 MHz, CD3CN, 27 °C) δ/ppm: 8.95 (s, 4H), 8.76 (d, 4H, J 8.1 Hz), 8.18-8.24 (m, 8H), 8.09 (br s, 4H), 7.85 (d, 4H, J 8.4 Hz), 7.57 (d, 4H, J 8.8 Hz), 7.50 (dd, 4H, J 1.4, 6.0 Hz), 7.01 (d, 4H, J 8.8 Hz), 3.86 (s, 6H). MS (ESI-TOF) [CdL2]+ m/z 496.1186 (Calcd. 496.1196), [CdL2+ClO4]+ m/z 1091.1817 (Calcd. 1091.1883). Anal.
Cafed. for C₆₀H₂₄CdCl₂N₂O₁₀ (1190.33): C, 60.54; H, 3.56; N, 7.06. Found: C, 60.32; H, 3.41; N, 6.85%.

**Synthesis of [RuL₂] (PF₆)₂ (4).** RuCl₃·3H₂O (20 mg, 0.076 mmol) and ligand L (33.6 mg, 0.076 mmol) were added to 20 mL of methanol and the solution was heated to reflux for 3 h. The brownish precipitate which formed was filtered off and air dried to give 38.5 mg of [RuCl₃L]. The product was suspended in methanol (20 mL) with 26.2 mg (0.06 mmol) of L, after which 4 drops of 4-ethylmorpholine was added and the mixture was heated to reflux for another 4 h. The resulting solution was allowed to cool and excess of aqueous NH₄PF₆ was added to the solution. The formed dark red precipitate was filtered and washed several times with water. The product was then re-dissolved in a minimal volume of acetonitrile and excess of diethyl ether was added to give a bright red product, 4, which was filtered and washed several times with diethyl ether. Yield 59% (57 mg).

**1H NMR (500 MHz, CDCl₃, 30 °C) δ/ppm:** 9.03 (br s, 4H), 8.66 (d, 4H, J 8.4 Hz), 8.25 (dt, 4H, J 1.9, 8.5 Hz), 7.96 (td, 4H, J 1.6, 7.9 Hz), 7.89 (dp, 4H, J 2.0, 8.5 Hz), 7.58 (dp, 4H, J 2.1, 8.9 Hz), 7.44 (br d, 4H, J 5.5 Hz), 7.19 (dd, 4H, J 0.5, 1.3, 6.4 Hz), 7.02 (dp, 4H, J 2.0, 8.7 Hz), 3.86 (s, 6H). MS (ESI-TOF) [RuL₂]⁺ m/z 490.1208 (Calcd. 490.1201), [RuL₂·2PF₆]⁺ m/z 1125.2049 (Calcd. 1125.2049). Anal. Calc. for C₆₀H₂₄F₂₂O₁₆P₂Ru (1270.01): C, 56.74; H, 3.33; N, 6.62. Found: C, 56.94; H, 3.49; N, 6.81%.

**Synthesis of [PtMeI₂] (5).** A solution of PtMeI (30 mg, 0.082 mmol) in chloroform (10 mL) was added to a chloroform solution (10 mL) of L (35.9 mg, 0.082 mmol), and the reaction mixture was stirred at 50 °C for 6 h. The resulting yellow solution was then concentrated and excess of n-hexane was added. The formed pale-yellow solid 5 was isolated, washed several times with n-hexane and dried in vacuum. Yield 79% (52 mg). The product was crystallized as yellow crystals by slow diffusion of hexane and excess of diethyl ether was added to give a bright red product, 5, which was filtered and washed several times with diethyl ether.

Further refinement details for 2. Perchlorate anions were modelled as disordered over two positions each, with their respective relative occupancies refined freely. Their geometries were restrained to be tetrahedral, with Cl···O 1.2- and O···Cl···O 1.3-distances tied to a free variable which was then also refined. One of the acetonitrile molecules was partially substituted by a dichloromethane molecule. Its geometry was restrained to be the same as that of a well-ordered acetonitrile molecule also present in the structure, while the C–Cl bond lengths of the dichloromethane component were restrained to be equal. The relative occupancies of these two disorder components were allowed to refine freely. Restraints were also applied to the anisotropic displacement parameters of the disordered parts.

Further refinement details for 3. One of the perchlorate anions was modelled as disordered over two positions with their relative occupancies refined freely. Its geometry was restrained to be tetrahedral, with Cl···O 1.2- and O···Cl···O 1.3-distances tied to a free variable which was also refined. Both the acetonitrile molecules in the structure were found to be disordered. Their geometries were fixed by restraining both 1.2- and 1.3-distances to the values obtained from Cambridge Structural Database. One of them was modelled with half-occupancy due to the disorder being around the inversion center, while the other one was modelled as two disorder components whose relative occupancies were allowed to refine freely. Restraints were also applied to the anisotropic displacement parameters of the disordered parts. Some reflections were obscured by the beam stop and were thus omitted from the refinement.

Further refinement details for 5. The anisotropic displacement parameters of the disordered parts had to be restrained. Some large residual electron density peaks still remained around the platinum and iodine atoms.

**Computational details**

The geometry of L was optimized using the PBE1PBE density functional26 together with Ahlrichs’ TZVP basis sets. Calculations were performed for the molecular ground state as well as for the first excited singlet state within the TD-DFT formalism. Vibrational frequencies were calculated using analytical (ground state) and numerical (excited state) methods to ensure that the stationary points correspond to true minima on the potential energy surface. The polarizable continuum model was used for the treatment of solvent effects. Vertical excitations/emissions with linear response solvation were considered without state-specific treatment of the solvent reaction field. Single point TD-DFT calculation was also performed for the complex 2 using crystal structure geometry and polarizable continuum model for the treatment of solvent (dichloromethane) effects. All calculations were done with the Gaussian09 program package for visualization of optimized geometries and molecular orbitals, the program GaussView was employed.

**Results and discussion**

The monoporphyrine ligand L was prepared via Sonogashira cross-coupling reaction between 4-((4-bromophenyl)-2',2'-bipyridine and 4-ethynylanisole in the presence of Pd(PPh₃)₄/Cul as a catalyst (Scheme 1). Metal (M) complexes of L were then synthesized (Scheme 2) in order to examine the binding of the ligand to different metal centers as well as to study the influence of metal coordination on the observed
photophysical properties. The Fe(II), Zn(II), and Cd(II) complexes 1-3 were obtained in 79-90% yield by reacting the tridentate ligand L with appropriate metal salts in 2:1 ratio. The Ru(II) complex 4 was synthesized by the stepwise addition of L to the metal center. The 1:1 reaction of L with RuCl$_3$·3H$_2$O in methanol afforded [RuCl$_3$L] which could be further reacted with another equivalent of L in methanol and in the presence of 4-ethylmorpholine as a reducing agent. Treatment of this solution with excess of ammonium hexafluorophosphate (in water) afforded the complex 4 as a bright red solid in 59% yield. The complex 5 was obtained in 79% yield by heating a chloroform solution containing trimethylplatinum(IV) iodide and L in 1:1 ratio.

The electrospray ionization mass spectra (ESI-MS) for the bis-ligand complexes 1-4 were consistent with the proposed [ML$_2$(X)$_2$] formulation (X = anion); all the complexes exhibited base peaks for the parent ion [ML$_2$] as well as peaks for singly charged ions [ML$_2$+X]$^+$. The ESI-MS analysis of 5 showed that the most abundant m/z value corresponds to the loss of iodide, giving [PtMe$_3$L]$^+$. In addition, the isotope patterns observed for each of the complexes 1-5 were consistent with those calculated for the formulated species.

1H NMR spectroscopy

The room temperature 1H NMR spectra of complexes 1-4 (in CD$_3$CN) are sharp, well resolved and show only one set of signals for the 2,2’:6’,2’’-terpyridine domain. This indicates that the terpyridine ligands coordinate to the metal centers in symmetric tridentate fashion. In contrast, the 1H NMR spectrum of complex 5 (in CD$_2$Cl$_2$) is severely broadened at room temperature, indicating the presence of a dynamic process with an exchange rate faster than the NMR timescale. A well resolved spectrum of 5 could, however, be obtained upon cooling the sample to -60 °C (see ESI†).

The platinum-methyl region of the low-temperature 1H NMR spectrum of 5 is comprised of three signals, each with two satellites due to $^{195}$Pt-H scalar coupling, consistent with the presence of three non-equivalent methyl groups: two in equatorial (Me$_A$ and Me$_B$) and one in axial (Me$_C$) environment (Fig. 1). This indicates that the terpyridine ligand in 5 is coordinated in bidentate fashion and that the ligand oscillates between equivalent bonding modes at higher temperatures. Although similar bidentate coordination has been reported

Scheme 1 Synthesis of the terpyridine ligand L.

Scheme 2 Synthesis of complexes 1-5.
before for the Pt(IV) complexes PtMe₂X(terpy) (X = Cl, I; terpy = 2,2’-6,2’’-terpyridine), the related [PtCl₄(Bu-terpy)]Cl (Bu-terpy = 4,4’’,4’’-tri-tert-butyl-2,2’’,6’,2’’’-terpyridine) salt contains a cation in which the ligand chelates the metal in tridentate fashion. The low temperature ¹H NMR spectrum of 5 also shows ten signals for the hydrogen nuclei of the terpyridine moiety, which further supports the bidentate binding mode. The ¹H coupling constant observed for the methyl group trans to the central pyridyl ring (Me₈) is greater than that for the methyl group trans to the terminal pyridyl ring (Me₉), suggesting that the central pyridinic nitrogen atom exerts greater trans influence and should therefore have a longer Pt–N bond (Table 2).

Crystallographic investigations

The structure of the ligand L: The monoterpyridine ligand L was crystallized as yellowish-orange crystals upon slow diffusion of chloroform into its methanol solution at room temperature. X-ray crystallographic data and structural refinement parameters of L are reported in Table 1. Selected bond lengths and angles are shown in Table 2.

The ligand L crystallizes in the monoclinic P2₁/c space group. The crystal structure of L (Fig. 2) shows that the pyridinic nitrogen atoms on the terpyridine moiety adopt a trans arrangement about the bonds C6–C7 and C9–C13. Such configuration is commonly found in the solid state structures of terpyridines; the C–N bond lengths [1.378(2) and 1.3503(18) Å] and C–H···N(pyridyl) (closest dimer distance is 3.360(2) Å) and 3.485(2) Å) and C−H···O(CH₃) (d(C··O = 3.238(2) Å) hydrogen bonds between neighboring molecules.

The crystal structures of 1-3: Single crystals of 1 and 3 were obtained by slow diffusion of diisopropyl ether into their acetonitrile solutions at room temperature; a 2:1 mixture of acetonitrile and dichloromethane was used in the case of complex 2. X-ray crystallographic data and structural refinement parameters of the complexes are listed in Table 1, whereas selected bond lengths and angles of the complexes are given in Table 2. Complexes 1-3 all crystallize in the triclinic space group P1. The crystal structures of 2 and 3 contain molecules of the crystallization solvent (acetonitrile) in the crystal lattice and the crystal structure of 3 contains two crystallographically independent cations in the unit cell.

The crystal structure of 1 confirms the anticipated 2:1 ligand to metal stoichiometry in the cation. The Fe(II) center shows distorted octahedral geometry in which the two terpyridine ligands occupy mer coordination sites (Fig. 4). The Fe–N bond distances involving the central pyridyl ring [1.879(2) and 1.885(2) Å] are significantly shorter than those to the terminal pyridyl rings [1.971(3) and 1.988(3) Å] (Table 2), which arises from the restricted bite angle of the terpyridine ligand. As a whole, the Fe–N bond distances are comparable with those reported for related Fe(II)-terpyridine complexes. The crystal structures of 2 and 3 show the formation of similar bis-complexes as in the case of 1 in which the metal centers (M) have a distorted MN₆ core (Fig. 4). All other key bond lengths and angles in 1-3 are similar to those reported for related Fe(II) and Zn(II)/Cd(II)-terpyridine complexes. The M–N bond distances increase from 1 to 3 due to the
increasing metal size (Table 2) which also leads to a decrease in the bite angle of the terpyridine ligand. The cations in 1-3 are all slightly bent around the C=C triple bond, similarly to the free ligand L, but the relative orientation of the aryl rings in the diphenylacetylene moiety differs significantly from the mean plane of the terpyridine framework with no regularity in the observed twist angles.

The crystal structure of 5: In order to confirm the bidentate chelate nature of the terpyridine ligand in 5, crystal structure of the complex was sought. Yellow crystals of 5 were obtained by slow diffusion of n-hexane into its dichloromethane solution at room temperature. X-ray crystallographic data and structural refinement parameters for 5 are reported in Table 1, whereas selected bond lengths and angles are given in Table 2.

Complex 5 crystallizes in the monoclinic P2₁/c space group and with adventitious solvent molecules (dichloromethane) in the crystal lattice. The asymmetric unit consists of two crystallographically independent complexes in which the Pt(IV) centers are hexacoordinated by three methyl groups in fac arrangement, an iodine atom, and the terpyridine ligand in a bidentate binding mode (Fig. 5). The Pt–N bond distance involving the central pyridyl ring is significantly (> 0.1 Å) longer than the Pt–N bond of the terminal pyridyl ring (Table 2) as predicted from the \(^3J_{Pt-H}\) coupling constants in the low temperature \(^1\)H NMR data. As a whole, the key bond lengths and bond angles of 5 are very much comparable to that reported for the related complex [PtMe₃I(terpy)]. With L acting as a bidentate ligand in 5, significant deviation from planarity is observed even for its terpyridine moiety. The two coordinated pyridyl rings are twisted from planarity by 19.1(4)° while the angle between the central and the non-coordinated pyridyl ring is significantly larger, 48.3(5)° (the corresponding torsion angles are 14.4(5)° and 40.6(5)° in the other crystallographically independent molecule in the unit cell). The packing of 5 is influenced by weak intra- and intermolecular hydrogen bonding involving the non-coordinated pyridyl ring, the methoxy substituent, the iodide ligand as well as the solvent molecules trapped in the crystal lattice.

![ORTEP plots](Image)

**Fig. 4** ORTEP plots of the cations present in the lattices of complexes 1 (top), 2, and 3 (bottom). Thermal ellipsoids are drawn at the 50% level. Hydrogen atoms, anions, and solvent molecules are omitted for clarity. In the case of 3, only one of the two crystallographically independent cations is shown.
Fig. 5 ORTEP plot of 5. Thermal ellipsoids are drawn at the 50% level and atom labelling is shown only for nitrogen atoms and the atoms directly bound to the platinum center. Hydrogen atoms and solvent molecules are omitted for clarity and only one of the two crystallographically independent molecules is shown.

Table 1 Crystallographic data for the ligand L and the metal complexes 1-3 and 5.

|  | L       | 1      | 2      | 3      | 5      |
|---|---------|--------|--------|--------|--------|
| CCDC No. | 941619 | 1008273| 1008274| 1008275| 1008276|
| empirical formula | C\textsubscript{64}H\textsubscript{42}N\textsubscript{6}O\textsubscript{6} | C\textsubscript{64}H\textsubscript{42}N\textsubscript{6}O\textsubscript{6} | C\textsubscript{64}H\textsubscript{42}N\textsubscript{6}O\textsubscript{6} | C\textsubscript{64}H\textsubscript{42}N\textsubscript{6}O\textsubscript{6} | C\textsubscript{64}H\textsubscript{42}N\textsubscript{6}O\textsubscript{6} |
| M\textsubscript{r}/g | 439.50 | 1232.98| 1232.65| 1221.08| 891.51 |
| T/K | 123(1) | 123(1) | 123(1) | 123(1) | 123(1) |
| \(\lambda/\AA\) | 0.71073 | 0.71073 | 1.54184 | 0.71073 | 1.54184 |
| crystal color, shape | Orange-yellow, block | purple, block | yellow, plate | yellow, plate | yellow, lath |
| crystal size/mm\(^3\) | 0.60×0.50×0.50 | 0.25×0.15×0.10 | 0.36×0.11×0.04 | 0.60×0.30×0.05 | 0.36×0.12×0.04 |
| crystal system | Monoclinic | triclinic | triclinic | triclinic | Monoclinic |
| space group | \(P2_1/c\) | \(P\overline{1}\) | \(P\overline{1}\) | \(P\overline{1}\) | \(P2_1/c\) |
| \(a/\AA\) | 16.6843(5) | 11.2130(3) | 11.0650(3) | 13.9688(2) | 10.96168(15) |
| \(b/\AA\) | 8.3034(3) | 13.5540(4) | 13.7517(7) | 17.2312(2) | 23.2974(7) |
| \(c/\AA\) | 16.3540(4) | 19.9336(7) | 23.0439(9) | 25.2477(4) | 25.7681(5) |
| \(\alpha^\circ\) | 90 | 79.9930(16) | 84.220(4) | 102.2197(9) | 90 |
| \(\beta^\circ\) | 103.3099(16) | 87.9424(18) | 79.057(3) | 99.7574(7) | 99.2317(15) |
| \(\gamma^\circ\) | 90 | 65.3545(16) | 87.837(4) | 109.5050(8) | 90 |
| \(V/\AA^3\) | 2204.77(12) | 2669.42(15) | 2805.62(2) | 5405.00(13) | 6495.39(19) |
| \(Z\) | 4 | 2 | 2 | 4 | 8 |
| \(\rho/gcm^{-3}\) | 1.324 | 1.534 | 1.459 | 1.501 | 1.823 |
| \(\mu/mm^{-1}\) | 0.082 | 0.448 | 2.212 | 0.572 | 17.302 |
| \(F(000)\) | 920 | 1264 | 1271 | 2490 | 3440 |
| \(\theta\) range/\(^\circ\) | 2.51 to 25.25 | 2.08 to 25.25 | 3.23 to 67.75 | 2.29 to 25.25 | 3.48 to 67.73 |
| completeness to \(b_{max}\) | 99.3\% | 99.7\% | 98.5\% | 99.7\% | 98.7\% |
| reflections collected | 9296 | 21832 | 15789 | 43577 | 20527 |
| independent reflections | 3948 \([R(int) = 0.0261]\) | 9631 \([R(int) = 0.0494]\) | 10005 \([R(int) = 0.0340]\) | 19498 \([R(int) = 0.0373]\) | 11610 \([R(int) = 0.0288]\) |
| absorption correction | multi-scan | multi-scan | multi-scan | numerical (gaussian) | |
| max. and min. transmission | 0.7457 and 0.6075 | 0.7457 and 0.6008 | 1.0000 and 0.8781 | 0.7457 and 0.5934 | 0.6490 and 0.0810 |
| refinement method | full-matrix least squares on \(F^2\) | full-matrix least squares on \(F^2\) | full-matrix least squares on \(F^2\) | full-matrix least squares on \(F^2\) | full-matrix least squares on \(F^2\) |
| data/restraints/parameters | 3948/3038 | 9377/30768 | 10005/506891 | 19504/3441559 | 11610/427665 |
| goodness-of-fit on \(F^2\) | 1.047 | 1.015 | 1.033 | 1.020 | 1.086 |
| final \(R\) indices \([I > 2\sigma(I)]\) | R1 = 0.0401, wR2 = 0.0968 | R1 = 0.0556, wR2 = 0.1082 | R1 = 0.0612, wR2 = 0.1667 | R1 = 0.0526, wR2 = 0.1130 | R1 = 0.0570, wR2 = 0.1424 |
| R indices (all data) | R1 = 0.0546, wR2 = 0.1054 | R1 = 0.0935, wR2 = 0.1257 | R1 = 0.0760, wR2 = 0.1829 | R1 = 0.0798, wR2 = 0.1277 | R1 = 0.0631, wR2 = 0.1470 |
| largest diff. peak and hole (eÅ\(^3\)) | 0.167 and -0.156 | 0.423 and -0.379 | 0.727 and -0.778 | 0.822 and -0.780 | 2.284 and -1.795 |
| Ligand L  | C2-N1 | 1.3342(18) | C7-N8 | 1.3430(18) | C13-N18 | 1.3490(18) |
|-----------|-------|------------|-------|------------|---------|------------|
| C6-N1     | 1.3503(18) | C9-N8 | 1.3451(17) | C17-N18 | 1.3403(19) |
| C6-C7     | 1.4865(19) | C9-C13 | 1.4904(19) | C11-C19 | 1.4875(19) |
| C22-C25   | 1.436(2) | C25-C26 | 1.201(2) | C26-C27 | 1.434(2) |
| C2-C3     | 1.382(2) | C4-C5 | 1.383(2) | C7-C12 | 1.3937(19) |
| C3-C4     | 1.387(2) | C5-C6 | 1.393(2) | C9-C10 | 1.3850(19) |
| C10-C11   | 1.395(2) | C30-O33 | 1.3648(17) | C34-O33 | 1.4278(19) |
| N1-C2-C3  | 123.94(14) | N1-C6-C5 | 122.12(3) | N1-C6-C7 | 116.11(12) |
| N8-C7-C12 | 122.65(13) | N8-C7-C6 | 116.58(12) | N8-C9-C10 | 122.68(13) |
| N8-C9-C13 | 116.38(12) | N18-C13-C14 | 122.25(13) | N18-C13-C9 | 116.93(12) |
| N18-C17-C16 | 123.83(14) | C2-N1-C6 | 117.57(12) | C7-N8-C9 | 117.78(12) |
| C17-N18-C13 | 117.25(12) | C30-O33-C34 | 118.36(12) | O33-C30-C31 | 124.72(13) |
| O33-C30-C29 | 115.36(13) | C26-C25-C22 | 175.13(16) | C25-C26-C27 | 178.94(16) |

| Complex 1  | Complex 2  | Complex 3* |
|------------|------------|------------|
| Fe1-N1A    | Zn1-N1A    | Cd1A-N1A   | 2.325(4) |
| Fe1-N1B    | Zn1-N1B    | Cd1A-N1B   | 2.345(4) |
| Fe1-N8A    | Zn1-N8A    | Cd1A-N8A   | 2.322(3) |
| Fe1-N8B    | Zn1-N8B    | Cd1A-N8B   | 2.295(3) |
| Fe1-N18A   | Zn1-N18A   | Cd1A-N18A  | 2.374(3) |
| Fe1-N18B   | Zn1-N18B   | Cd1A-N18B  | 2.340(4) |
| N1A-Fe1-N8A | N1A-Zn1-N8A | N1A-Cd1A-N8A | 70.21(13) |
| N1A-Fe1-N18A | N1A-Zn1-N18A | N1A-Cd1A-N18A | 138.91(12) |
| N1A-Fe1-N1B | N1A-Zn1-N1B | N1A-Cd1A-N1B | 98.79(13) |
| N1A-Fe1-N8B | N1A-Zn1-N8B | N1A-Cd1A-N8B | 114.53(12) |
| N1A-Fe1-N18B | N1A-Zn1-N18B | N1A-Cd1A-N18B | 96.05(13) |
| N8A-Fe1-N1A | N8A-Zn1-N1A | N8A-Cd1A-N1A | 68.87(11) |
| N8A-Fe1-N1B | N8A-Zn1-N1B | N8A-Cd1A-N1B | 117.49(12) |
| N8A-Fe1-N8A | N8A-Zn1-N8B | N8A-Cd1A-N8B | 170.93(12) |
| N8A-Fe1-N8B | N8A-Zn1-N8B | N8A-Cd1A-N8B | 101.93(12) |
| N8A-Fe1-N18A | N8A-Zn1-N18A | N8A-Cd1A-N18A | 102.96(13) |
| N8A-Fe1-N18B | N8A-Zn1-N18B | N8A-Cd1A-N18B | 105.54(11) |
| N8A-Fe1-N1B    | N8A-Zn1-N1B    | N8A-Cd1A-N1B    | 88.83(12) |
| N1B-Fe1-N8A   | N1B-Zn1-N1A   | N1B-Cd1A-N1A   | 70.23(12) |
| N1B-Fe1-N18A  | N1B-Zn1-N1B   | N1B-Cd1A-N1B   | 140.54(12) |
| N1B-Fe1-N1B   | N1B-Zn1-N1B   | N1B-Cd1A-N1B   | 70.33(12) |
| C22A-C25A-C26A | C22A-C25A-C26A | C22A-C25A-C26A | 174(5) |
| C25A-C26A-C27A | C25A-C26A-C27A | C25A-C26A-C27A | 177(6) |
| C22B-C25B-C26B | C22B-C25B-C26B | C22B-C25B-C26B | 174(5) |
| C25B-C26B-C27B | C25B-C26B-C27B | C25B-C26B-C27B | 178(5) |

| Complex 5  | Pt1A-N1A   | 2.151(7) | Pt1B-N1B | 2.127(8) | Pt1A-IIA | 2.7505(8) |
|------------|------------|---------|----------|---------|----------|------------|
| Pt1-N8A    | 2.252(7) | Pt1-N8B | 2.256(8) | Pt1B-N8B | 2.7892(10)|
| Pt1A-C35A  | 2.061(11) | Pt1A-C36A | 2.054(9) | Pt1A-C37A | 2.069(10)|
| Pt1B-C35B  | 2.046(12) | Pt1B-C36B | 2.048(12) | Pt1B-C37B | 2.135(13)|
| N1A-Pt1A-N8A | 76.2(2) | N1A-Pt1A-IIA | 87.87(19) | N8A-Pt1A-IIA | 96.24(18)|
| C35A-Pt1A-N1A | 176.9(3) | C36A-Pt1A-N1A | 95.4(4) | C37A-Pt1A-N1A | 92.7(3)|
| C35A-Pt1A-N8A | 101.3(3) | C36A-Pt1A-N8A | 168.5(3) | C37A-Pt1A-N8A | 85.6(3)|
| C35A-Pt1A-IIA | 94.3(3) | C36A-Pt1A-IIA | 91.23(3) | C37A-Pt1A-IIA | 178.2(3)|
| C36A-Pt1A-C35A | 86.8(4) | C36A-Pt1A-C37A | 87.14(4) | C35A-Pt1A-C37A | 85.2(4)|
| N1B-Pt1B-N8B | 76.1(3) | N1B-Pt1B-IIB | 86.62(3) | N8B-Pt1B-IIB | 95.65(19)|
| C35B-Pt1B-N1B | 175.9(5) | C36B-Pt1B-N1B | 97.4(5) | N1B-Pt1B-C37B | 92.2(4)|
| C35B-Pt1B-N8B | 102.3(4) | C36B-Pt1B-N8B | 171.7(4) | C37B-Pt1B-N8B | 86.1(3)|

* Data is given for only one of the two crystallographically independent molecules in the unit cell.
Absorption spectroscopy and DFT calculations

The room temperature UV-Vis spectrum of L (in dichloromethane) shows absorption maxima at 322 nm (extinction coefficient $4.48 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) along with a shoulder at 298 nm (extinction coefficient $4.12 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) (Fig. 6). The absorption maxima of L is influenced only marginally by change in solvent polarity (Table 3, see ESI†) and is considerably red-shifted compared to that of 4´-phenyl-2,2´:6,2´´-terpyridine (278 nm in dichloromethane),11d 4´-(4-methoxyphenyl)-2,2´:6,2´´-terpyridine (285 nm in dichloromethane),11d and 4´-[(1,1´-biphenyl)-4-yl]-2,2´:6,2´´-terpyridine (289 nm in ethanol).11c That the monoterpyridine ligand L absorbs at higher wavelength in comparison to the mentioned terpyridines can be explained with the morphology of its frontier orbitals (Fig. 7) and the rigidity of the conjugated linkage between the diphenylacetylene moiety and the central pyridyl ring of the terpyridine fragment.12a,12b

DFT calculations (at the PBE1PBE/TZVP level) were conducted to provide insight into the electronic structure of the ligand L. The optimized structure of L (see ESI†) was found to be in very good agreement with the X-ray data, the only exception being the twist angle between the terpyridine and ethynylanisole moieties. This difference can, however, be attributed to the omission of crystal packing interactions in calculations conducted for isolated molecules in the gas phase. The vertical excitation energies of L were subsequently calculated with time dependent TD-DFT formalism using the optimized molecular coordinates and the PBE1PBE/TZVP functional/basis set combination.

In good agreement with the experimental data (Table 3), the TD-DFT calculation for L in the gas phase reveals two excitations between 275 and 400 nm with significant oscillator strengths. The most intense band involves the HOMO→LUMO excitation at 347 nm, whereas the other transition appears as a shoulder at 289 nm and has the biggest contribution form the HOMO→LUMO+2 excitation (see ESI†). The frontier Kohn-Sham orbitals of L relevant to the calculated absorption at 347 nm are shown in Fig. 7. It is immediately evident that the HOMO→LUMO transition is clearly of π→π* type and involves an intramolecular transfer of electron density from the diphenylacetylene moiety (HOMO) to the terpyridine framework (LUMO). The HOMO of L is essentially the HOMO of free 1,2-diphenylacetylene (see ESI†), whereas the LUMO of L is a linear combination of orbitals from both the diphenylacetylene and terpyridine fragments. The electronic structure of L is therefore a hybrid of its constituents, which is clearly reflected in its fluorescence properties that are quite unlike to other monoterpyridine ligands known to date (see below).

Table 3 Photophysical properties of L in different solvents and in the solid state

| System  | $\lambda_{\text{max}}^{\text{abs}}$ (nm)$^a$ | $\lambda_{\text{max}}^{\text{em}}$ (nm)$^b$ | $\tau_\text{f}$ (ns)$^c$ | $\Phi_{\text{F}}$† |
|--------|------------------|------------------|------------------|------------------|
| THF    | 324              | 406              | 1.24             | 0.66             |
| DCM    | 322              | 411              | 1.35             | 0.78             |
| CH$_3$CN | 320             | 436              | 1.75             | 0.82             |
| DMF    | 324              | 436              | 1.69             | 0.86             |
| EtOH   | 321              | 439              | 1.90             | 0.78             |
| MeOH   | 322              | 452              | 1.87             | 0.57             |
| solid state &sol; | -               | 428              | 1.32             | -                |

$^a$Lowest energy absorption band. $^b$Upon excitation of the lowest energy absorption band. $^c$Fluorescence lifetime. $^d$Relative fluorescence quantum yield.

The influence of solvent effects to the calculated absorption properties was also tested by performing calculations on the solute placed in a cavity within the solvent reaction field (either acetonitrile or dichloromethane, see ESI†). The results show that solvent effect modelled with an implicit solvent model changes the calculated absorption wavelength only by 5 nm, in agreement with the insensitivity of the experimental absorption maximum to the used solvent (Table 3).

Fig. 6 UV-Vis absorption spectra of the terpyridine ligand L and its metal complexes 1-5 in dichloromethane (25 °C).

Fig. 7 Isosurface plots of the highest occupied Kohn-Sham molecular orbital (HOMO, top) and lowest unoccupied Kohn-Sham molecular orbital (LUMO, bottom) of L calculated at the PBE1PBE/TZVP level of theory.

Fig. 6 also shows the UV-Vis spectra of complexes 1-5 measured in dichloromethane at room temperature. Significant changes are observed in the spectrum of L upon complex formation. Most notably, the UV region of the absorption spectra is clearly dominated by spin-allowed ligand-centered (LC) π→π* transition(s) at around 340 nm. The transitions observed for complexes 1-4 in the wavelength range 360-380 nm are presumably of metal induced intra-ligand charge transfer (ILCT) type as discussed recently in the case of related...
Zn(II)-terpyridine complexes.\textsuperscript{37d} We tested this by calculating the transitions for 2 at the PBE1PBE/TZVP level using the TD-DFT formalism and the crystal structure geometry of the salt. The calculations reveal several high-intensity absorptions in between 300 and 400 nm of which the most intense appear at 340 and 399 nm. As expected, these two transitions involve intra-ligand excitations from the diphenylacetylene moiety to the terpyridine framework (primarily from HOMO and HOMO-2 to LUMO and LUMO+1, see ESI\textsuperscript{†}). The complexes 1 and 4 also exhibit typical metal to ligand charge-transfer (MLCT) transitions in the visible region of the spectra. The MLCT bands for 1 and 4 are observed at 574 and 497 nm, respectively, and are very close to those reported for [Fe(biphterpy)]:\textsuperscript{23} (571 nm) and [Ru(biphterpy)]:\textsuperscript{24} (494 nm) (biphterpy = 4´-(biphenylene)-2,2´:6,2´´-terpyridine) in the literature.\textsuperscript{25} Although the LC and MLCT transitions are not influenced by solvent polarity, the ILCT bands of complexes 1-4 become increasingly broadened when using highly polar solvents.

**Emission spectroscopy and DFT calculations**

The ligand L displays bright blue emission upon irradiation by UV light. Upon excitation of the absorption maximum of L at 322 nm in dichloromethane, a single intense band is observed in the recorded emission spectrum, indicating that the fluorescence involves only one excited state. To probe the fluorescence properties of L further, its emission spectrum was recorded in different solvents and the results are summarized in Table 3 (see ESI\textsuperscript{†}). Even though the absorption maximum of L was mostly unperturbed by the polarity of the solvent, its emission maximum displays significant solvatochromism (Fig. 8). This suggests that the first excited state of the monoterpyridine ligand L has a relatively high dipole moment compared to the ground state.

![Fig. 8 Emission spectra of L in different solvents (25 °C).](Image)

The ligand L displays relatively high quantum yield in a range of different solvents (Table 3). Mono-terpyridine ligands rarely possess good emissive characteristics and to the best of our knowledge, L has one of the highest quantum yields (\(\Phi_F = 0.85\)) in N,N-dimethylformamide) reported so far for any terpyridine compound of its kind.\textsuperscript{11c, 12a} Surprisingly, the fluorescence of L is only mildly affected even in polar protic solvents such as ethanol and methanol, a result which is in stark contrast to literature reports on analogous terpyridine ligands such as 4´-(4,N,N-dimethylaminophenyl)-2,2´:6,2´´-terpyridine\textsuperscript{11g} and 6-amino-2,2´:6,2´´-terpyridines.\textsuperscript{11a, 11b}

Studying the fluorescence decay behavior of L in different solvents shows that its fluorescence lifetime increases with the polarity of the solvent. The ligand L retains its fluorescence also in the solid state.\textsuperscript{38} Many fluorescent compounds, particularly \(\pi\) conjugated systems, lose their emissive properties in the solid state due to increasing intermolecular interactions that induce non-radiative deactivation pathways.\textsuperscript{39} In case of L, the molecules form \(\pi\)-stacked dimers in the solid state structure and the weak \(\pi\)→\(\pi\) interactions between the adjacent terpyridine moieties (Fig. 3) do not have any significant influence to the parts of the molecule responsive of the observed fluorescence (see below).

DFT geometry optimizations (at PBE1PBE/TZVP level) conducted for the first excited state of the ligand L show that its structure is in many respects very similar to that of the ground state (see ESI\textsuperscript{†}). The most notable difference is the shortening of the C11–C19 bond that connects the terpyridine unit to the diphenylacetylene moiety from 1.475 to 1.445 Å (gas phase data). In addition, the ligand twists to a conformation in which all of its pyridyl and phenyl rings are nearly coplanar. These changes are consistent with the morphology of the LUMO of L which shows increased conjugation between the central pyridyl ring and the diphenylacetylene moiety (Fig. 7). As discussed earlier, the frontier orbitals of L indicate that significant internal charge transfer takes place upon electronic excitation, which readily explains the change in the calculated dipole moment from 1.9 to 13.7 D, thereby rationalizing the relatively large Stokes shift observed for L in highly polar environments (Table 3).

TD-DFT calculations conducted for the first excited state of L predict an emission wavelength of 393 nm in the gas phase. The inclusion of solvent effect with an implicit solvent model changes the calculated emission wavelength to 439 (dichloromethane) and 447 nm (acetonitrile). These data are in reasonable agreement with the experimentally determined emission maximum of L in different solvent systems (Table 3). The LUMO of L (Fig. 7) shows that the electronic excitation involves an orbital with virtually no contribution from atoms of the terminal pyridyl and phenyl rings. This differs considerably from the morphology of the LUMO of the parent terpyridine ligand (see ESI\textsuperscript{†}) and offers a plausible explanation as to why L shows such a high quantum yield in different environments. Typically molecules that have high degree of flexibility show poor fluorescence properties due to promotion of non-radiative decay pathways. In case of L, the orbital most relevant to its fluorescence properties displays extended \(\pi\)-conjugation and is fully confined to a structurally rigid part in the molecular skeleton. In contrast, in typical terpyridine systems the lowest excitation is of singlet \(\pi\)→\(\pi^*\) type, which causes a rapid intersystem crossing to a triplet \(\pi\)→\(\pi^*\) state and no fluorescence of the terpyridine is observed.\textsuperscript{12}

![Fig. 9 Fluorescence of L (2.5 × 10^{-5} M in dichloromethane) in the presence of different divalent metal ions (0.5 eq. as perchlorate salts in acetonitrile) under UV-lamp (365 nm) at 25 °C.](Image)
Fig. 9 shows the effect of coordination to different divalent transition metal ions on the fluorescence of the terpyridine ligand L. It is evident that the fluorescence of L becomes completely quenched upon adding metals such as Mn$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Hg$^{2+}$, whereas the addition of Zn$^{2+}$ and Cd$^{2+}$ (that is, complexes 2 and 3) results in greenish-yellow fluorescence (see ESI†). However, compared to the free ligand L, the Zn(II) and Cd(II) complexes show only weak fluorescence with an emission maximum at longer wavelengths (Fig. 10).

The quenching of ligand fluorescence by transition metal ions during complex formation is a rather common phenomenon. A transition-metal center can induce quenching through electron transfer or energy transfer mechanisms. Upon complexation with terpyridines, the Ru(II) complexes produce a MLCT type singlet excited state, 1MLCT, which quickly gives rise to the corresponding triplet state, 3MLCT. The 3MLCT state is short lived due to efficient thermally activated decay via a proximal 3d-d state. For this reason, no fluorescence is observed for Ru(II) (or Fe(II)) complexes of terpyridines. In case of Zn(II) or Cd(II) complexes, the filled d$^{10}$ shell makes the metals inoffensive from a photophysical point of view as they cannot be involved in an electron transfer processes nor do they show redox activity required for photo-induced electron transfer. Hence, in Zn(II) and Cd(II) systems, fluorescence from ILCT type excited states to the ground state is readily observed.

Table 4 gives a summary of the photophysical properties of 2 and 3 in different solvents. The emission maxima of both complexes is red-shifted with increasing solvent polarity, which is consistent with the ILCT state being the excited state. Significant quenching is observed in solvents of high polarity as indicated by the fluorescence quantum yields. The fluorescence lifetimes of 2 and 3 follow the aforementioned trend. The metal complexes 2 and 3 show noticeable green fluorescence also in the solid state with a considerably longer fluorescence lifetime than that found for L (1.32 ns).

Although 2 and 3 exhibit fluorescence in solution and in the solid state, complexes 1, 4 and 5 are non-fluorescent irrespective of the environment. It should also be mentioned that complex 5 is soluble to most polar aprotic solvents but only sparingly soluble in protic solvents such as methanol and ethanol. In addition, at higher dilutions in these solvents, extensive dissociation of the complex takes place for which reason its emission spectra shows the characteristics of the free ligand.

### Table 4 Photophysical properties of 2 and 3 in different solvents and in the solid state

| Complex | System | $\lambda_{\text{max}}^{\text{abs}}$ (nm)$^a$ | $\lambda_{\text{max}}^{\text{em}}$ (nm)$^a$ | $\tau_F$ (ns)$^b$ | $\Phi_F$ | $\Phi_C$ |
|---------|--------|-----------------|-----------------|----------------|--------|
| 2       | DCM   | 377             | 542             | 2.02           | 0.19   | -      |
|         | THF   | 367             | 535             | 1.46           | 0.11   | -      |
|         | CH$_2$CN | 365         | 572             | 0.85           | 0.03   | -      |
|         | Solid-state | -        | 505             | 4.37           | -      | -      |
| 3       | DCM   | 374             | 532             | 1.88           | 0.21   | -      |
|         | THF   | 368             | 524             | 1.35           | 0.16   | -      |
|         | CH$_2$CN | 365         | 565             | 0.78           | 0.03   | -      |
|         | Solid-state | -        | 523             | 4.33           | -      | -      |

$^a$ Absorbance of the lowest energy absorption band. $^b$ Upon excitation of the lowest energy absorption band. $^c$ Fluorescence lifetime. $^d$ Relative fluorescence quantum yield.

### Conclusions

In conclusion, a new hybrid luminescent fluorophore 4’-[4-{4-methoxyphenyl}ethynyl]phenyl]-2,2’:6’,2′-terpyridine ligand L, constructed by combining the diphenylacetylene moiety with the terpyridine framework, is described together with its structural and photophysical properties. Several transition metal complexes of L were also synthesized and characterized in detail. The structural investigations show that the ligand binds to common divalent metal ions in tridentate fashion but forms a bidentate complex with trimethylplatinum(IV) iodide. The synthesized ligand is highly emissive in both solid state and in non-polar solutions, and retains its efficiency even in polar organic media - a property that is unique among monoterpyridine ligands. Results from density functional theory calculations associate the luminescence of L to an intraligand charge transfer state that involves electronic excitation from the diphenylacetylene moiety to the terpyridine framework. The influence of metal coordination on the photophysical properties of L has also been investigated. Although the Fe(II), Ru(II) and Pt(IV) complexes of L do not show any fluorescence, its Zn(II) and Cd(II) complexes exhibit strong green luminescence with significant solvatochromism. The new fluorescent ligand L and its Zn and Cd complexes are currently being investigated for their use in optoelectronics.

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### Notes and references

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