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PAPER

Comparative structural and spectral analyses for mononuclear and dinuclear metal complexes of 2-thiophen and 2-(5-bromothiophen)imidazo[4,5-f][1,10]phenanthroline†

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A series of mononuclear and dinuclear mercury(I), mercury(II), nickel(II), lanthanum(III), ferrous(II) and ruthenium(II) complexes **4–11** with different metal/ligand molar ratios (1 : 1, 1 : 2 and 1 : 3), having 2-thiophenimidazo[4,5-f][1,10]phenanthroline (TIP) and 2-(5-bromothiophen)imidazo[4,5-f][1,10]phenanthroline (5-Br-TIP) ligands, have been synthesized and structurally compared. In addition, three protonated salts of TIP and 5-Br-TIP (**1–3**) with PF₆[−] and ClO₄[−] counterions have been described herein where the proton is found to be located at one of the nitrogen atoms of 1,10-phenanthroline moiety. It is notable that the whole molecules of dinuclear mercury(I) and nickel(II) complexes **6** and **7** exhibit excellent planarity in the lengths of 2.52 and 2.90 nm, respectively. UV-Vis, ¹H NMR and luminescence spectra of ligands TIP and 5-Br-TIP, protonated salts **1–3** and metal complexes **4–11** have also been studied and compared.

Introduction

Recently, investigations on the heteroaromatic compounds bearing donor–acceptor subunits have attracted much attention.^{1,2} In particular, coordination chemistry of 1,10-phenanthroline (phen) derivatives with extended π -system has become a hot topic of research. These metal complexes have shown certain potential applications in photonics, optoelectronics, solar cells and molecular probes and so on,^{3–8} mainly because of their essential structural advantages: 1) bidentate chelating nitrogen atoms in the rigid structure that are easily coordinated with metal centers; 2) a large delocalized π -system which usually exhibits good optical and electronic properties; 3) abundant substituent positions for finely tuning their chemical and physical properties. Among a variety of 1,10-phenanthroline derivatives, imidazo[4,5-f][1,10]phenanthroline grafted by different heteroaromatic rings have been an important class because of their symmetrical and asymmetrical structures as well as pH

dependency and luminescence sensitivity. Moreover, the imidazole-containing phenanthroline ligands are constituted by parts of both electron acceptors and electron donors, which may tune the ground and excited state properties of the complexes.^{9–17} Some transition-metal complexes bearing these ligands have been reported, in which Ji, Chao, and their co-workers focused on the investigations on polypyridine ruthenium(II) complexes for their NLO effects, luminescent and biological properties.^{18–23}

Our previous research in this area has been mainly focused on the linear 3,8-extended 1,10-phenanthroline-based heterocyclic aromatic fluorescence compounds showing semiconducting, photoresponsive and chemosensing properties.²⁴ Among them, a 3,8-oligothiophene substituted 1,10-phenanthroline compound with a molecular length of 3.3 nm has been synthesized and structurally characterized.^{24b} In this paper, we have tried to extend 1,10-phenanthroline's π -system at its 5 and 6 positions by introducing an electron-donating thiophene group onto the electron-withdrawing imidazo[4,5-f][1,10]phenanthroline unit and further extend the molecular planarity and size by the formation of coordinative bonds with suitable metal centers. As a result, two planar ligands with large delocalized π -system have been successfully prepared: namely 2-thiophenimidazo[4,5-f][1,10]phenanthroline (TIP) and 2-(5-bromothiophen)imidazo[4,5-f][1,10]phenanthroline (5-Br-TIP).

By using these two compounds, seven mononuclear and dinuclear coordination complexes with mercury(I, II), nickel(II), lanthanum(III), ferrous(II) and ruthenium(II) metal centers as well as three protonated salts are prepared and characterized. They are formulated as [H(TIP)](PF₆)(CH₃OH) (**1**), [H(5-Br-TIP)](ClO₄)(H₂O)₂ (**2**), [H(5-Br-TIP)](ClO₄)(C₂H₅OH) (**3**), [Hg(TIP)I₂](CH₃OH)₂ (**4**), [Hg(5-Br-TIP)I₂](DMF) (**5**),

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† Electronic supplementary information (ESI) available: Selected bond lengths and bond angles, hydrogen bonding interactions, powder X-ray diffraction experimental and computer-simulated patterns, UV-Vis absorption, ¹H NMR and fluorescence excitation spectra for ligands TIP/5-Br-TIP and their protonated salts and metal complexes. CCDC reference numbers 887806–887815 for compounds **1–10**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce26001h

[Hg₂(TIP)₂](ClO₄)₂ (**6**), [Ni₂(5-Br-TIP)₂Cl₄(CH₃OH)₂] (**7**), [La(5-Br-TIP)₂(NO₃)₃](C₂H₅OH)₂ (**8**), [Fe(TIP)₃]₂(ClO₄)₄(C₂H₅OH)₂(H₂O)₅ (**9**), [Ru(bpy)₂(TIP)]₃(PF₆)₆(CH₃OH)₂(H₂O)₁₃ (**10**) and [Ru(bpy)₂(5-Br-TIP)](PF₆)₂ (**11**) (DMF = *N,N'*-dimethylformamide, bpy = 2,2'-bipyridine). Among them, **6** and **7** are dinuclear complexes exhibiting excellent planarity with the whole molecular lengths of 2.52 and 2.90 nm, respectively. Various intramolecular and intermolecular interactions at the supramolecular level are discussed for these complexes. Additionally, UV-Vis, ¹H NMR and luminescence spectra of ligands TIP and 5-Br-TIP, protonated salts **1–3** and metal complexes **4–11** have been studied and compared. As far as we are aware, there is only one Pb(II) complex of ligand TIP in literature with regard to the structural report on ligands TIP/5-Br-TIP and their protonated salts and metal complexes.²⁵

Experimental section

Materials and physical measurements

All the reagents were of analytical grade from commercial sources and were used without any further purification. Ligands TIP and 5-Br-TIP were prepared according to the literature method with high yields.²⁶

Elemental analyses were measured with a Perkin-Elmer 1400 °C analyzer. Infrared spectra (IR, 4000–400 cm⁻¹) were collected on a Nicolet FT-IR 170X spectrophotometer at 25 °C using KBr plates. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan MAT SSQ 710 mass spectrometer in a scan range 100–1200 amu. Ultraviolet-visible (UV-Vis) spectra were recorded on a Shimadzu UV-3600 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm at room temperature. Luminescence spectra were recorded on an F-4600 fluorescence spectrophotometer at room temperature (25 °C) using the same solutions as those for the UV-Vis determination. ¹H NMR spectroscopic measurements were performed on a Bruker AM-500 NMR spectrometer, using TMS (SiMe₄) as an internal reference at room temperature. The powder X-ray diffraction (XRD) patterns were recorded on crushed single crystals in the 2θ range 5–55°. The XRD measurements were performed on a Philips X'pert MPD pro X-ray diffractometer using Cu-Kα radiation, in which the X-ray tube was operated at 40 kV and 40 mA at room temperature.

Caution! Although no problem was encountered in all our experiments, transition metal perchlorates are potentially explosive and should be handled in small quantities.

Syntheses of compounds 1–11

General synthetic procedure for compounds of 1–9. Ligand TIP/5-Br-TIP and NH₄PF₆/NaClO₄·H₂O or certain metal salt were placed in a thick-walled Pyrex tube (*ca.* 25 cm long). After the addition of certain solvent (and one drop of concentrated hydrochloric acid in the cases of protonated salts **1**, **2** and **3**), the mixture was treated in an ultrasonicator for one minute and was frozen with liquid N₂, then evacuated under a vacuum and sealed with a torch. The tube was then placed inside an oven at 100 °C under solvothermal reaction conditions for 4 days to furnish the crystals of compounds **1–9**.

[H(TIP)](PF₆)(CH₃OH) (**1**). Ligand TIP (30.2 mg, 0.10 mmol), NH₄PF₆ (19.6 mg, 0.12 mmol) and 2.5 mL methanol were used and **1** was isolated in a yield of 31.8 mg (66.3%) based on ligand TIP. Anal. Calcd. for [C₁₈H₁₅F₆N₄O₃S]: C, 45.01; H, 3.15; N, 11.66%. Found: C, 44.77; H, 3.40; N, 11.31%. Main FT-IR absorptions (KBr pellets, cm⁻¹): 3466.5(s), 3412.9(s), 3040.2(w), 2926.2(w), 1637.3(m), 1610.1(m), 1441.1(m), 845.5(vs), 622.7(s), 479.6(m). UV-Vis (CH₃OH): λ_{max} = 329, 294 and 236 nm. Negative ESI-MS peaks (*m/z*): 302 ([TIP]⁻), 334 ([TIP(CH₃OH)]⁻). ¹H NMR (500 MHz, DMSO-*d*₆) δ: 14.25 (s, 1H, NH), 9.17 (m, 4H, phen), 8.19 (dd, 2H, *J* = 7.9 and 4.9 Hz, phen), 7.95 (d, 1H, *J* = 3.4 Hz, thiophene), 7.83 (d, 1H, *J* = 4.9 Hz, thiophene), 7.33 (t, 1H, thiophene).

[H(5-Br-TIP)](ClO₄)(H₂O)₂ (**2**). Ligand 5-Br-TIP (38.1 mg, 0.10 mmol), NaClO₄·H₂O (15.4 mg, 0.11 mmol) and 2.5 mL water were used and **2** was isolated in a yield of 31.1 mg (60.0%) based on ligand 5-Br-TIP. Anal. Calcd. for [C₁₇H₁₄BrClN₄O₆S]: C, 39.44; H, 2.73; N, 10.82%. Found: C, 39.22; H, 2.60; N, 11.07%. Main FT-IR absorptions (KBr pellets, cm⁻¹): 3550.3(s), 3475.1(s), 3413.4(s), 3235.9(w), 3048.9(w), 1637.3(m), 1618.0(m), 1577.5(m), 1409.7(w), 1145.5(s), 1089.6(s), 809.9(w), 626.7(s), 489.8(m). UV-Vis (CH₃OH): λ_{max} = 328, 291 and 246 nm. Negative ESI-MS peaks (*m/z*): 381 ([5-Br-TIP]⁻), 417 ([5-Br-TIP)(H₂O)₂]⁻, 515 ([5-Br-TIP)(ClO₄)(H₂O)₂]⁻. ¹H NMR (500 MHz, DMSO-*d*₆) δ: 14.81 (s, 1H, NH), 9.25 (d, 2H, *J* = 8.2 Hz, phen), 9.13 (dd, 2H, *J* = 4.8, 1.0 Hz, phen), 8.17 (dd, 2H, *J* = 8.2, 4.9 Hz, phen), 7.87 (d, 1H, *J* = 3.9 Hz, thiophene), 7.39 (d, 1H, *J* = 3.9 Hz, thiophene).

[H(5-Br-TIP)](ClO₄)(C₂H₅OH) (**3**). Ligand 5-Br-TIP (38.1 mg, 0.10 mmol), NaClO₄·H₂O (15.4 mg, 0.11 mmol) and 2.5 mL ethanol were used and **3** was isolated in a yield of 20.4 mg (38.6%) based on ligand 5-Br-TIP. Anal. Calcd. for [C₁₉H₁₆BrClN₄O₅S]: C, 43.24; H, 3.06; N, 10.62%. Found: C, 42.99; H, 2.98; N, 10.92%. Main FT-IR absorptions (KBr pellets, cm⁻¹): 3417.2(s), 3045.0(w), 2998.8(w), 2935.1(w), 2859.9(w), 2796.3(w), 1610.3(m), 1571.7(s), 1542.8(m), 1486.8(s), 1351.9(m), 1085.7(vs), 809.9(s), 721.2(s), 617.1(m), 460.9(m). UV-Vis (CH₃OH): λ_{max} = 328, 291 and 246 nm. Negative ESI-MS peaks (*m/z*): 381 ([5-Br-TIP]⁻), 427 ([5-Br-TIP)(C₂H₅OH)]⁻, 515 ([5-Br-TIP)(ClO₄)(H₂O)₂]⁻.

[Hg(TIP)I₂](CH₃OH)₂ (**4**) and [Hg₂(TIP)₂](ClO₄)₂ (**6**). Ligand TIP (30.2 mg, 0.10 mmol), HgI₂ (45.4 mg, 0.10 mmol) and 2.5 mL methanol were used and yellow crystals of **4** was isolated in a yield of 34.6 mg (42.2%) based on ligand TIP. Anal. Calcd. for [C₁₉H₁₈HgI₂N₄O₂S]: C, 27.80; H, 2.21; N, 6.83%. Found: C, 27.48; H, 2.51; N, 7.05%. Main FT-IR absorptions (KBr pellets, cm⁻¹): 3432.5(b, s), 3032.2(w), 2940.4(w), 1645.2(s), 1650.2(m), 1420.6(m), 810.2(s), 622.4(m), 482.1(m). UV-Vis (CH₃OH): λ_{max} = 329, 294 and 209 nm. Only a few colorless needle crystals of **6** were obtained in the tube as a by-product (yield <5%).

[Hg(5-Br-TIP)I₂](DMF) (**5**). Ligand 5-Br-TIP (38.1 mg, 0.10 mmol), HgI₂ (45.4 mg, 0.10 mmol) and a mixture of 1.0 mL ethanol and 2.0 mL DMF were used and yellow crystals of **5** was isolated in a yield of 48.2 mg (53.1%) based on ligand 5-Br-TIP. Anal. Calcd. for [C₂₀H₁₆BrHgI₂N₅O₃S]: C, 26.43; H, 1.77; N,

7.71%. Found: C, 26.09; H, 1.56; N, 7.90%. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3444.7(b, s), 3286.5(w), 3072.5(w), 2920.1(w), 2866.1(w), 1654.8(vs), 1571.9(m), 1485.1(s), 1353.9(m), 1085.9(w), 806.2(s), 731.0(s), 702.1(w). UV-Vis (CH_3OH): $\lambda_{\text{max}} = 330, 297$ and 208 nm. ^1H NMR (500 MHz, DMSO-d_6): δ : 14.14 (s, 1H, NH), 9.08 (d, 2H, $J = 3.5$ Hz, phen), 9.01 (d, 2H, $J = 24.6$ Hz, phen), 8.14 (d, 2H, $J = 31.6$ Hz, phen), 7.66 (d, 1H, thiophene), 7.39 (d, 1H, $J = 3.6$ Hz, thiophene).

$[\text{Ni}_2(5\text{-Br-TIP})_2\text{Cl}_4(\text{CH}_3\text{OH})_2]$ (**7**). Ligand 5-Br-TIP (38.1 mg, 0.10 mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (23.8 mg, 0.10 mmol) and 3.0 mL methanol were used and green crystals of **7** was isolated in a yield of 27.5 mg (50.6%) based on ligand 5-Br-TIP. Anal. Calcd. for $[\text{C}_{36}\text{H}_{26}\text{Br}_2\text{Cl}_4\text{N}_8\text{Ni}_2\text{O}_2\text{S}_2]$: C, 39.82; H, 2.41; N, 10.32%. Found: C, 39.28; H, 2.32; N, 10.98%. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3303.5(s), 3068.2(s), 1610.3(m), 1571.7(m), 1486.8(s), 1405.8(m), 1355.7(s), 1087.6(m), 1008.6(s), 919.9(w), 819.6(m), 732.8(s), 700.0(m), 428.1(w). UV-Vis (CH_3OH): $\lambda_{\text{max}} = 329, 298$ and 208 nm.

$[\text{La}(5\text{-Br-TIP})_2(\text{NO}_3)_3](\text{C}_2\text{H}_5\text{OH})_2$ (**8**). Ligand 5-Br-TIP (38.1 mg, 0.10 mmol), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (21.7 mg, 0.05 mmol) and 3.0 mL ethanol were used and yellow crystals of **8** was isolated in a yield of 36.6 mg (62.1%) based on ligand 5-Br-TIP. Anal. Calcd. for $[\text{C}_{38}\text{H}_{30}\text{Br}_2\text{LaN}_{11}\text{O}_{11}\text{S}_2]$: C, 38.69; H, 2.56; N, 13.06%. Found: C, 38.44; H, 2.82; N, 13.35%. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3473.2(m), 3446.2(m), 3093.3(w), 2979.5(w), 1619.9(w), 1573.6(m), 1486.8(s), 1396.2(m), 1295.9(s), 1083.8(m), 1027.9(m), 811.9(m), 736.7(m), 707.7(m), 628.7(w), 418.5(w). UV-Vis (CH_3OH): $\lambda_{\text{max}} = 330, 297$ and 205 nm. ^1H NMR (500 MHz, DMSO-d_6): δ : 13.92 (s, 2H, NH), 9.02 (d, 4H, $J = 3.0$ Hz, phen), 8.79 (d, 4H, $J = 7.2$ Hz, phen), 7.82 (s, 4H, phen), 7.68 (d, 2H, $J = 3.8$ Hz, thiophene), 7.39 (d, 2H, $J = 3.9$ Hz, thiophene).

$[\text{Fe}(\text{TIP})_3]_2(\text{ClO}_4)_4(\text{C}_2\text{H}_5\text{OH})_2(\text{H}_2\text{O})_5$ (**9**). Ligand TIP (36.2 mg, 0.12 mmol), $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (14.5 mg, 0.04 mmol) and a mixture of 1.5 mL ethanol and 1.5 mL water were used and red crystals of **9** was isolated in a yield of 23.4 mg (46.6%) based on ligand TIP. Anal. Calcd. for $[\text{C}_{106}\text{H}_{82}\text{Cl}_4\text{Fe}_2\text{N}_{24}\text{O}_{23}\text{S}_6]$: C, 50.81; H, 3.30; N, 13.42%. Found: C, 50.52; H, 3.11; N, 13.66%. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3423.5(b, s), 3070.5(m), 2866.1(w), 1654.8(s), 1577.7(m), 1483.2(m), 1363.6(m), 1120.6(vs), 1083.9(vs), 850.6(m), 808.1(m), 723.3(m), 624.9(s). UV-Vis (CH_3OH): $\lambda_{\text{max}} = 527, 491, 329, 320, 296$ and 247 nm.

Preparation of ruthenium(II) complexes 10 and 11. To a stirred solution of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (24.2 mg, 0.05 mmol) in methanol (5 mL) was added a solution of ligand TIP (15.1 mg, 0.05 mmol) or ligand 5-Br-TIP (19.1 mg, 0.05 mmol) in methanol (5 mL). The resulting mixture was refluxed for 48 h and cooled to room temperature. An aqueous solution of excess NH_4PF_6 was then added, and the precipitate was removed by filtration, washed with water and a small amount of EtOH and Et_2O , recrystallized from methanol and dried in a vacuum to produce the red microcrystals of **10** and **11**, respectively.

$[\text{Ru}(\text{bpy})_2(\text{TIP})]_3(\text{PF}_6)_6(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_{13}$ (**10**). Yield: 18.8 mg (33.2%). Main FT-IR absorptions (KBr pellets, cm^{-1}): 3440.8(b, s), 3080.2(w), 1625.9(m), 1604.7(m), 1446.5(s),

1363.6(m), 840.9(vs), 761.8(s), 723.3(m), 557.4(s). UV-Vis (CH_3OH): $\lambda_{\text{max}} = 461, 425, 330, 289$ and 243 nm. Positive ESI-MS peaks (m/z): 358 ($[\text{Ru}(\text{bpy})_2(\text{TIP})]^{2+}/2$), 715 ($[\text{Ru}(\text{bpy})_2(\text{TIP-H})]^+$). ^1H NMR (500 MHz, DMSO-d_6): δ : 14.47 (s, 1H, NH), 9.01 (d, 2H, $J = 8.2$ Hz, phen), 8.84 (dd, 4H, $J = 19.0, 8.2$ Hz, bpy), 8.20 (t, 2H, bpy), 8.09 (t, 2H, bpy), 8.03 (d, 2H, $J = 5.1$ Hz, phen), 7.96 (d, 1H, $J = 3.4$ Hz, thiophene), 7.90 (dd, 2H, $J = 7.8, 5.6$ Hz, phen), 7.82 (d, 2H + 1H, $J = 5.2$ Hz, bpy + thiophene), 7.57 (m, 4H, bpy), 7.32 (m, 2H + 1H, bpy + thiophene). Single crystals of **10** suitable for X-ray diffraction measurement were grown from a mixture of methanol and water by slow evaporation in air at room temperature for 2 weeks.

$[\text{Ru}(\text{bpy})_2(5\text{-Br-TIP})](\text{PF}_6)_2$ (**11**). Yield: 16.2 mg (29.9%). Main FT-IR absorptions (KBr pellets, cm^{-1}): 3413.4(m), 3083.6(m), 2958.3(w), 2929.3(w), 1618.0(m), 1604.5(m), 1579.4(w), 1488.8(m), 1446.3(m), 1363.4(m), 842.7(vs), 761.7(s), 730.9(m), 557.3(s). UV-Vis (CH_3OH): $\lambda_{\text{max}} = 461, 338, 289$ and 208 nm. Positive ESI-MS peaks (m/z): 398 ($[\text{Ru}(\text{bpy})_2(5\text{-Br-TIP})]^{2+}/2$), 793 ($[\text{Ru}(\text{bpy})_2(5\text{-Br-TIP-H})]^+$). ^1H NMR (500 MHz, DMSO-d_6): δ : 8.98 (d, 2H, $J = 8.1$ Hz, phen), 8.84 (dd, 4H, $J = 19.1, 8.2$ Hz, bpy), 8.21 (t, 2H, bpy), 8.10 (t, 2H, bpy), 8.02 (d, 2H, $J = 3.6$ Hz, phen), 7.89 (dd, 2H, $J = 8.2, 6.7$ Hz, phen), 7.84 (d, 2H, $J = 5.5$ Hz, bpy), 7.74 (d, 1H, $J = 3.8$ Hz, thiophene), 7.59 (t, 4H, bpy), 7.44 (d, 1H, $J = 3.6$ Hz, thiophene), 7.34 (t, 2H, bpy).

Crystallography

Single-crystal samples of **1–10** were covered with glue and mounted on glass fibers and used for data collection. Crystallographic data of **1–10** were collected at 291(2) K on a Bruker SMART 1 K CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences using XPREP. Absorption corrections were performed to all data and the structures were solved by direct methods and refined by full-matrix least-squares method on F^2_{obs} by using the SHELXTL-PC software package.²⁷ All non-H atoms were anisotropically refined and all hydrogen atoms were inserted in the calculated positions, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. Some of the PF_6^- , ClO_4^- anions and some thiophen rings are refined disorderedly with different site occupancy factors. The summary of the crystal data, experimental details and refinement results for **1–10** is listed in Table 1. Selected bond distances and bond angles related to the central metal ions for **4–10** are given in Table S11 \dagger , while O–H \cdots O, N–H \cdots O and C–H \cdots O types of hydrogen bonding interactions in **1–10** are listed in Table S12. \dagger

Results and discussion

Synthetic, spectral and structural aspects

Syntheses and spectral characterizations. In our experiments, protonated salts **1**, **2** and **3** were firstly obtained as by-products from the reactions between transition-metal salts with different counterions and ligands TIP and 5-Br-TIP. After that, preparative

Table 1 Crystallographic data and structural refinements for compounds 1–10

Compound	1	2	3	4	5
Formula	C ₁₈ H ₁₅ F ₆ N ₄ OPS	C ₁₇ H ₁₄ BrClN ₄ O ₆ S	C ₁₉ H ₁₆ BrClN ₄ O ₅ S	C ₁₉ H ₁₈ HgI ₂ N ₄ O ₂ S	C ₂₀ H ₁₆ BrHgI ₂ N ₅ OS
Formula weight	480.38	517.74	527.78	820.83	908.74
<i>T</i> /K	291(2)	291(2)	291(2)	291(2)	291(2)
Crystal size (mm)	0.10 × 0.12 × 0.12	0.10 × 0.11 × 0.12	0.10 × 0.11 × 0.12	0.10 × 0.10 × 0.12	0.10 × 0.10 × 0.12
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	6.919(3)	9.325(8)	15.333(11)	7.562(2)	7.666(2)
<i>b</i> /Å	21.908(10)	10.985(9)	8.370(8)	14.037(4)	24.296(3)
<i>c</i> /Å	14.415(5)	11.008(9)	17.857(13)	22.806(7)	14.862(2)
α (°)	90	99.61(2)	90	90	90
β (°)	112.97(2)	105.84(1)	111.57(3)	105.568(4)	116.268(5)
γ (°)	90	109.49(2)	90	90	90
<i>V</i> /Å ³	2011.7(15)	980.4(14)	2131(3)	2332.0(12)	2482.3(6)
ρ /g cm ⁻³ / <i>Z</i>	1.586/4	1.754/2	1.645/4	2.338/4	2.432/4
<i>F</i> (000)	976	520	1064	1512	1664
μ /mm ⁻¹	0.314	2.384	2.192	9.359	10.404
Max./min. <i>h</i> , <i>k</i> , <i>l</i>	7/−8, 26/−19, 17/−17	7/−11, 13/−10, 13/−13	17/−18, 9/−9, 21/−14	8/−8, 16/−16, 27/−15	8/−9, 25/−28, 17/−17
Collected refs	9845	4938	9567	11 676	12 456
Unique refs	3506	3377	3716	4084	4351
Refs [<i>I</i> > 2 σ (<i>I</i>)]	1556	1939	2822	2617	3012
Parameters	336	284	283	266	282
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0752/0.1866	0.0780/0.2234	0.0487/0.1275	0.0345/0.0630	0.0381/0.0816
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1414/0.2124	0.1240/0.2969	0.0614/0.1330	0.0589/0.0675	0.0574/0.0862
GOF on <i>F</i> ²	0.85	1.06	0.99	0.79	0.88
Max./min. $\Delta\rho$ /e Å ⁻³	0.41/−0.32	0.95/−1.28	0.60/−0.59	0.77/−0.84	0.89/−0.89
Compound	6	7	8	9	10
Formula	C ₃₄ H ₂₀ Cl ₂ Hg ₂ N ₈ O ₈ S ₂	C ₃₆ H ₂₆ Br ₂ Cl ₄ N ₈ Ni ₂ O ₂ S ₂	C ₃₈ H ₃₀ Br ₂ LaN ₁₁ O ₁₁ S ₂	C ₁₀₆ H ₈₂ Cl ₄ Fe ₂ N ₂₄ O ₂₃ S ₆	C ₁₁₃ H ₁₀₉ F ₃₆ N ₂₄ O ₁₅ P ₆ Ru ₃ S ₃
Formula weight	1204.80	1085.77	1179.58	2505.88	3312.48
<i>T</i> /K	291(2)	291(2)	291(2)	291(2)	291(2)
Crystal size (mm)	0.09 × 0.09 × 0.10	0.10 × 0.10 × 0.12	0.10 × 0.11 × 0.12	0.10 × 0.11 × 0.11	0.10 × 0.10 × 0.12
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>I</i> 2 ₁ 2 ₁
<i>a</i> /Å	9.8723(8)	8.186(2)	25.896(5)	18.229(5)	20.2150(11)
<i>b</i> /Å	9.9382(8)	10.332(2)	9.846(2)	18.329(5)	20.9756(12)
<i>c</i> /Å	10.7007(16)	12.858(2)	18.182(3)	19.533(5)	33.8400(19)
α (°)	91.615(2)	109.506(2)	90	62.294(3)	90
β (°)	102.813(2)	93.424(2)	110.564(2)	76.676(4)	90
γ (°)	119.470(1)	102.044(2)	90	68.310(4)	90
<i>V</i> /Å ³	879.54(17)	992.6(3)	4340.3(14)	5355(2)	14 348.9(14)
ρ /g cm ⁻³ / <i>Z</i>	2.275/1	1.816/1	1.805/4	1.554/2	1.533/4
<i>F</i> (000)	570	540	2328	2572	6676
μ /mm ⁻¹	9.055	3.382	2.995	0.574	0.534
Max./min. <i>h</i> , <i>k</i> , <i>l</i>	11/−11, 9/−11, 15/−15	9/−9, 12/−9, 13/−15	24/−30, 11/−11, 21/−13	21/−11, 21/−20, 23/−20	24/−17, 24/−24, 40/−35
Collected refs	4526	4998	10 655	26 740	36 761
Unique refs	3063	3434	3819	18 456	12 633
Refs [<i>I</i> > 2 σ (<i>I</i>)]	1925	2371	3393	8770	7049
Parameters	253	254	297	1490	920
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0336/0.0424	0.0387/0.0937	0.0239/0.0602	0.1154/0.3431	0.0567/0.1244
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0664/0.0471	0.0603/0.0991	0.0278/0.0613	0.1827/0.3682	0.1080/0.1359
GOF on <i>F</i> ²	0.74	0.91	1.03	1.08	0.96
Max./min. $\Delta\rho$ /e Å ⁻³	0.48/−0.63	0.66/−0.36	0.76/−0.69	1.28/−0.71	0.59/−0.26

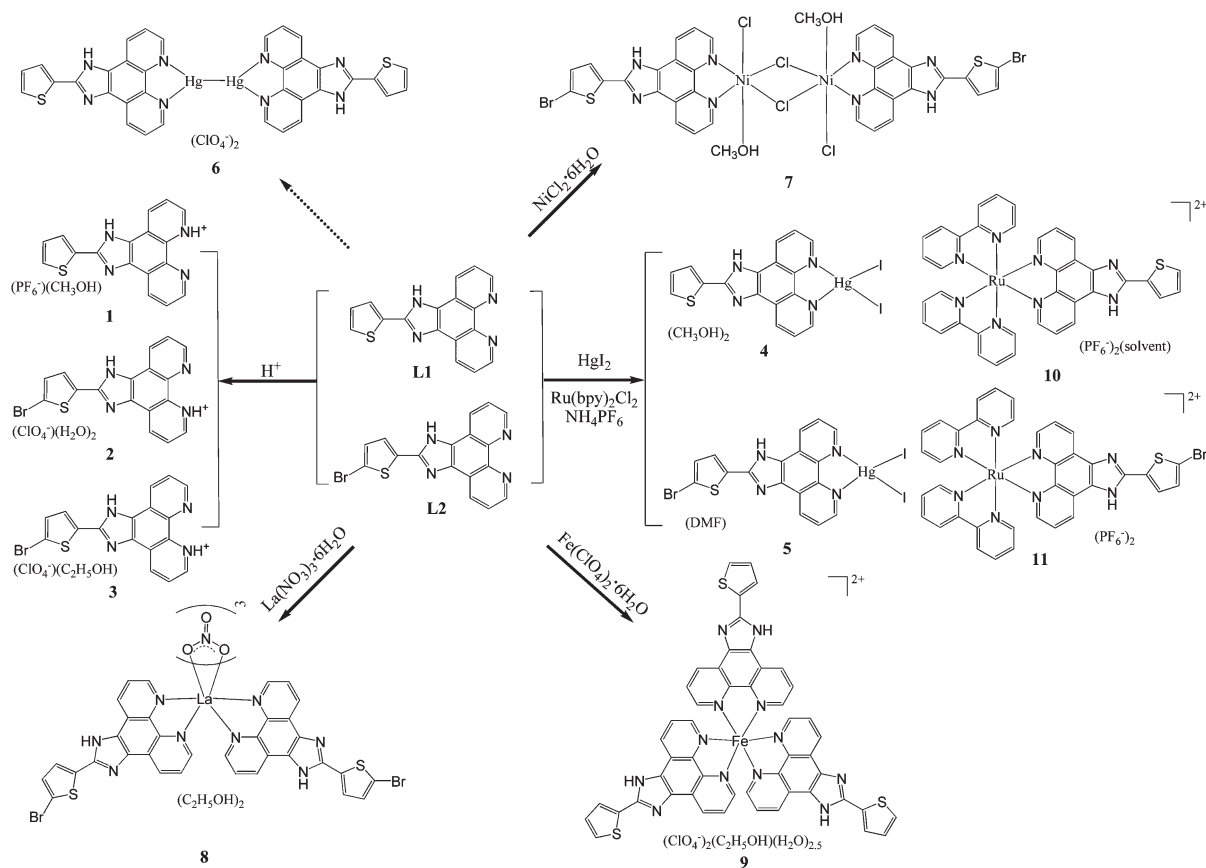
$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

experiments have been carried out by using ligands TIP and 5-Br-TIP and corresponding anions directly under acidic conditions to synthesize the protonated salts 1–3 in satisfactory yields.

In the synthesis of metal complexes 4–11 of TIP and 5-Br-TIP, different metal/ligand molar ratios have been employed from 1 : 1 to 1 : 3. However, as shown in Scheme 1, most of the products proved to be 1 : 1 complexes, and only one La(III) complex 8 with a 1 : 2 molar ratio and one Fe(II) complex 9 with a 1 : 3 molar ratio have been obtained. It is suggested that the nature of the metal center such as charge, radii, coordination geometry and electronic structure as well as the presence of

different counterions may play important roles in altering the molar ratios of products.

Single crystals of Hg(I) complex 6 were obtained as a by-product in the process of synthesizing Hg(II) complex 4, where a reduction reaction from Hg(II) to Hg(I) species is supposed to take place. Nevertheless, control experiments have been attempted by using Hg(I) salts to react directly with ligand TIP, but the products are very complicated and no pure complex 6 can be isolated. In addition, single crystals of 2 are found to easily undergo efflorescence when exposed to air. In the cases of Ru(II) complexes 10 and 11, we failed to obtain the single-crystal



Scheme 1 Syntheses of compounds 1–11 starting from ligands TIP and 5-Br-TIP.

structure of **11**, but we have accomplished other characterizations including ^1H NMR spectral comparisons with **10**.

To confirm the structures of the bulk materials, powder X-ray diffraction experiments have been carried out to verify the pure phase of complexes. As shown in Fig. S11†, it can be confirmed that the bulk synthesized materials are homogeneous for their single-crystal structures. From the FT-IR spectra, strong and sharp peaks are found at 1084–1090 and 841–846 cm^{-1} for related compounds (**1–3**, **6**, and **9–11**), corresponding to the typical absorptions of PF_6^- and ClO_4^- counterions, respectively. UV-vis absorption spectra of free ligands TIP/5-Br-TIP and compounds **1–11** (except **3** and **6**) have been recorded in the wavelength range of 200–800 nm in CH_3OH (1.0×10^{-5} M) at room temperature. As shown in Fig. S12-1† and Fig. S12-2†, the absorption band profiles for TIP, **1**, **4**, **9** and **10** as well as 5-Br-TIP, **2**, **5**, **7**, **8** and **11** at high-energy band are similar where two absorptions could be found corresponding to the π - π^* transition of the ligands. The relative absorption intensities are decreased after the protonation of ligands, as can be seen in Table 2. With regard to the Ru(II) complexes **10** and **11**, a new peak centered at 461 nm is observed, which can be assigned as the metal ligand charge transfer (MLCT). In the case of 1 : 3 Fe(II) complex **9**, the MLCT peak is observed at 527 nm.

The ^1H NMR spectra of TIP and 5-Br-TIP as well as **1**, **2**, **5**, **8**, **10** and **11** are shown in Fig. S13†. The ^1H NMR data have been rearranged into two groups in Fig. 1a and Fig. 1b with the same abscissa to compare the differences among the free ligands,

protonated salts and coordinative complexes. It is notable that the protons in the protonated salts are obviously shifted toward the lower fields in comparison with the free ones. For example, the chemical shifts of thiophene protons have been shifted from 7.90, 7.75 and 7.28 ppm in free ligand TIP to 7.95, 7.83 and 7.33 ppm in protonated salt **1**, while those have been shifted from 7.66 and 7.39 ppm in free ligand 5-Br-TIP to 7.88 and 7.39 ppm in protonated salt **2** (Fig. 1a). For complex **5**, the signals of crystalline DMF protons have been detected at 7.94, 2.72 and 2.87 ppm.²⁸ As for the two Ru(II) complexes **10** and **11**, analogous ^1H NMR spectra have been recorded although no single-crystal structure of **11** is present. However, the chemical shifts of thiophene protons have also been shifted to the lower

Table 2 UV-vis and fluorescence emission spectral data of ligands TIP/5-Br-TIP and compounds 1–11

Compound	$\lambda_{\text{abs, max}}$ (nm)	$\log \epsilon$	$\lambda_{\text{em, max}}$ (nm)	Intensity _(a.u.)
TIP	294	4.64	516	1353
5-Br-TIP	342	4.87	497	1238
1	294	4.39	516	1361
2	291	4.50	514	1266
4	294	4.74	511	2064
5	330	4.63	510	2044
7	329	4.85	505	46
8	329	4.84	517	2828
9	296	5.12	516	811
10	289	5.01	611	1006
11	289	4.51	609	1002

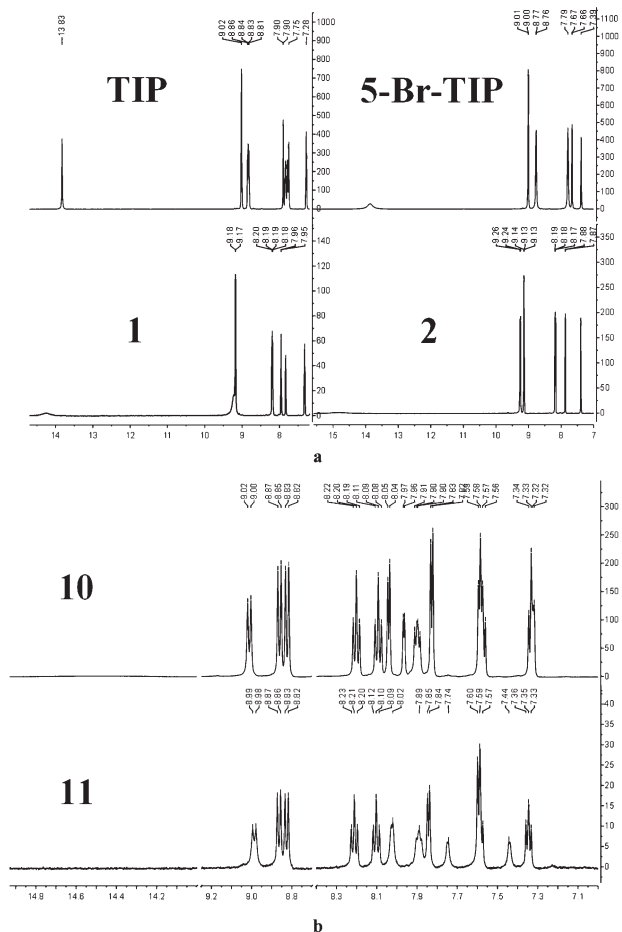


Fig. 1 ^1H NMR spectra of compounds **1**, **2**, **10** and **11** in $\text{DMSO}-d_6$ together with those of ligands TIP and 5-Br-TIP for comparison.

fields (7.96, 7.82 and 7.32 ppm in **10** and 7.74 and 7.44 in **11**) in comparison with free ligands TIP and 5-Br-TIP, as shown in Fig. 1b.

The luminescence spectra of compounds **1–11** (except **3** and **6**), together with free ligands TIP and 5-Br-TIP for comparison, have been investigated in methanol (1.0×10^{-5} M) at room

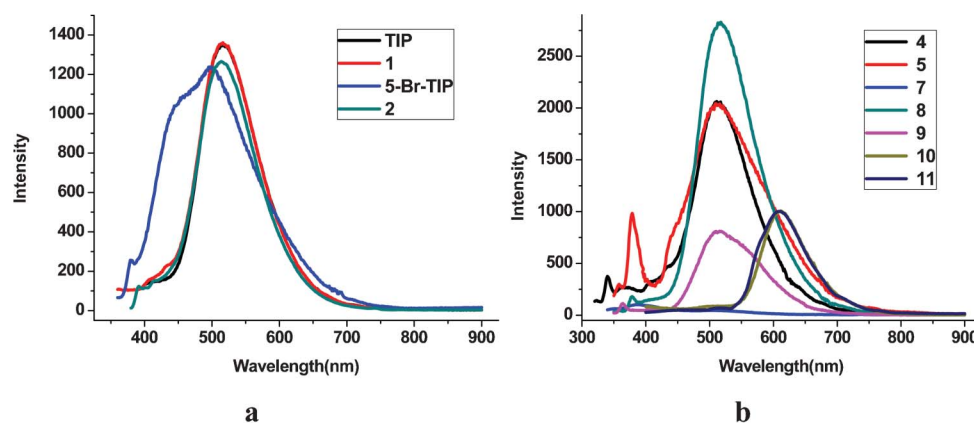


Fig. 2 Fluorescence emission spectra of ligands TIP and 5-Br-TIP as well as their protonated salts and metal complexes in the solution of CH_3OH (1.0×10^{-5} M).

temperature. As can be seen in Fig. 2a and Fig. S14†, free ligands TIP and 5-Br-TIP display luminescence emissions at $\lambda_{\text{max}} = 516$ and 497 nm in methanol upon excitation at $\lambda_{\text{ex}} = 304$ and 340 nm. In contrast, protonated salts **1** and **2** exhibit fluorescence emissions at $\lambda_{\text{max}} = 516$ and 514 nm upon excitation at $\lambda_{\text{ex}} = 303$ and 368 nm, respectively. Nearly no shift has been observed between TIP and **1**, while a red shift of 17 nm has been detected between 5-Br-TIP and **2**. Therefore, the luminescence properties of 5-Br-TIP are more sensitive to the protonation of ligand. For the d^{10} mercury(II) complexes **4** and **5**, fluorescence emissions are observed at $\lambda_{\text{max}} = 511$ and 510 nm upon excitation at $\lambda_{\text{ex}} = 305$ and 338 nm, respectively, and the fluorescence intensities are both increased as shown in Fig. 2b. Little difference is observed in the maximum fluorescence emissions even if different TIP and 5-Br-TIP ligands are present in **4** and **5**. However, the fluorescence quenching effect has been detected in the case of d^8 nickel(II) complex **7**. As for the d^0 lanthanum(III) complex **8**, the luminescence emission is observed at $\lambda_{\text{max}} = 517$ nm upon excitation at $\lambda_{\text{ex}} = 338$ nm. The fluorescence intensity is further enhanced in **8** compared with the two mercury(II) complexes, mainly because of the chelation of two 5-Br-TIP ligands. For the d^6 iron(II) complex **9**, luminescence emissions are observed at $\lambda_{\text{max}} = 516$ nm upon excitation at $\lambda_{\text{ex}} = 325$ nm, where the luminescence intensity is decreased severely although three TIP ligands are chelated to the central cation. It is noted that the fluorescence emissions of Ru(II) complexes **10** and **11** are recorded at $\lambda_{\text{max}} = 612$ and 609 nm upon excitation at $\lambda_{\text{ex}} = 335$ and 341 nm, respectively, where large red-shifts of 96 and 112 nm are found after metal-ion complexation.

Structural descriptions of compounds 1–10. [$H(\text{TIP})$](PF_6)(CH_3OH) (**1**). Complex **1** is a hexafluorophosphate of protonated TIP, as shown in Fig. 3-1. The asymmetric unit contains one TIP molecule with one proton on the N1 atom, one PF_6^- counterion and one methanol molecule. The whole protonated TIP molecule exhibits good planarity with a small dihedral angle of $1.9(2)^\circ$ between the two aromatic rings. As a result, strong π - π stacking interactions are found between neighboring cations in the packing structure (Fig. 5-1). The centroid-centroid distances of neighboring imidazole rings are only 3.495 and 3.536 Å, respectively. In addition, strong

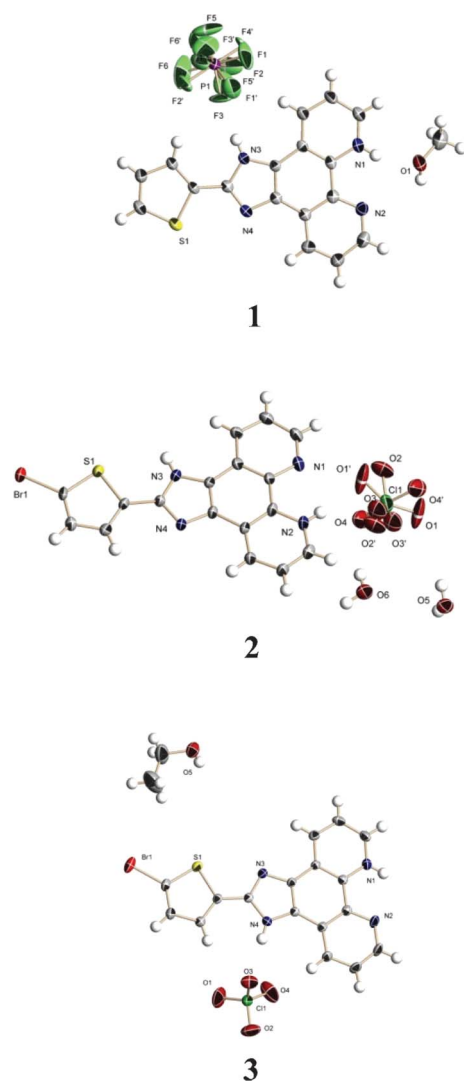


Fig. 3 ORTEP plots of the protonated salts 1–3. The thermal ellipsoids are drawn at 30% probability.

hydrogen-bonding interactions are found between the hydrogen atom of protonated N1 atom and the oxygen atom (O1) of crystalline methanol molecule.

$[H(5\text{-Br-TIP})](ClO_4)(H_2O)_2$ (**2**) and $[H(5\text{-Br-TIP})](ClO_4)(C_2H_5OH)$ (**3**). Both compounds **2** and **3** are perchlorates of protonated 5-Br-TIP. The asymmetric structure of **2** with the anisotropic displacement ellipsoids and atom numbering scheme is shown in Fig. 3-2, including one 5-Br-TIP with one proton added on the N2 atom, one counter anion of ClO_4^- and two free water molecules. **2** crystallizes in the triclinic space group $P\bar{1}$, and the dihedral angle between the adjacent imidazole and thiophene ring of 5-Br-TIP is $5.1(9)^\circ$. In contrast, **3** crystallizes in the monoclinic space group $P2_1/c$ and one uncoordinated ethanol molecule is included in the asymmetric unit of **3** instead of two free water molecules in **2** (Fig. 3-3). The dihedral angle between the adjacent imidazole and thiophene ring of 5-Br-TIP in **3** is lowered to $1.4(3)^\circ$, exhibiting better planarity than **2**.

A lot of strong π - π stacking interactions as well as p - π stacking interactions are found between the aromatic rings and bromine atoms of the neighboring cations in **2**, as shown in Fig. 5-2. Moreover, abundant intramolecular and intermolecular hydrogen-bonding interactions are found in the packing structure of **2** because of the presence of a large amount of hydrogen-bonding donors and acceptors. Different from **2**, weaker and fewer π - π stacking interactions, intramolecular and intermolecular hydrogen-bonding interactions are found in the crystal packing of **3** (Fig. 5-3). Moreover, no p - π stacking interactions are found between the aromatic rings and the bromine atoms in **3**.

$[Hg(TIP)I_2](CH_3OH)_2$ (**4**). The molecular structure of **1** : **1** mononuclear Hg(II) complex **4** with the atom-numbering scheme is shown in Fig. 4-4. It consists of one Hg(II) ion, one chelating TIP ligand, two coordinated iodine anions and two uncoordinated methanol molecules. The coordination geometry of the central Hg(II) center is a four-coordinate tetrahedron. The dihedral angle between the adjacent imidazole and thiophene ring is $1.1(2)^\circ$, which is the smallest value in this paper. Several π - π stacking interactions are observed on both sides of the planar TIP ligand in the packing structure, as shown in Fig. 5-4.

$[Hg(5\text{-Br-TIP})I_2](DMF)$ (**5**). Complex **5** is also a **1** : **1** mononuclear Hg(II) complex as shown in Fig. 4-5, consisting of one Hg(II) ion, one chelating 5-Br-TIP ligand, two coordinated iodine anions and one DMF molecule free of coordinative bond in the asymmetric unit. It crystallizes in the monoclinic space group $P2_1/c$ and the coordination geometry of the Hg(II) center is a four-coordinate tetrahedron. However, the dihedral angle between the adjacent imidazole and thiophene ring is $9.4(2)^\circ$, which is much larger than that in complex **4**. As shown in Fig. 5-5, π - π stacking interactions are observed only at one side of ligand 5-Br-TIP, which might cause the larger torsion of the C–C bond between the imidazole and the thiophene rings.

$[Hg_2(TIP)_2](ClO_4)_2$ (**6**). Complex **6** is a **1** : **1** dinuclear Hg(I) complex with a Hg(I)–Hg(I) bond as shown in Fig. 4-6. The asymmetric unit is composed of one Hg(I) ion, one chelating TIP ligand and one perchlorate anion. The coordination geometry for each central Hg(I) ion is a three-coordinate planar triangle. The Hg(I)–Hg(I) bond length is $2.514(1)$ Å, which is comparable with reported Hg(I) complexes.²⁹ The dihedral angle between the adjacent imidazole and thiophene ring is $1.4(2)^\circ$ and the mean deviation from the two TIP least-squares planes in this dinuclear complex is only $0.003(2)$ Å. Thus, the whole cation exhibits excellent planarity and linearity with a length of 2.52 nm. Moreover, π - π stacking interactions are found between neighboring layers of these cations, resulting in an extremely regular packing pattern, and the interlayer distances are only 3.312 – $3.338(2)$ Å (Fig. 5-6).

$[Ni_2(5\text{-Br-TIP})_2Cl_4](CH_3OH)_2$ (**7**). The molecular structure of **1** : **1** dinuclear Ni(II) complex **7** with anisotropic displacement ellipsoids and atom-numbering scheme is shown in Fig. 4-7. In comparison with other complexes, **7** consists of two Ni(II) ions, two chelating 5-Br-TIP ligands, two μ_2 -bridged chlorine anions, two mono-coordinated chlorine anions and two mono-coordinated

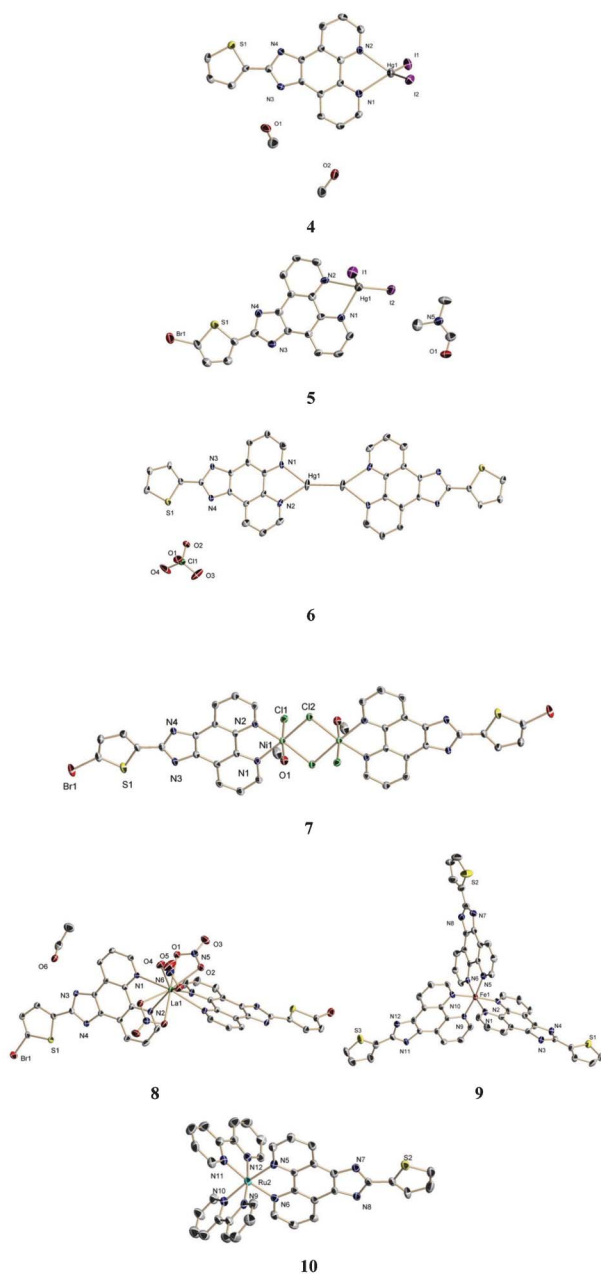


Fig. 4 ORTEP plots of metal complexes **4–10**. The thermal ellipsoids are drawn at 30% probability (hydrogen atoms are omitted for clarity).

methanol molecules. It crystallizes in the triclinic space group $P\bar{1}$ and the coordination geometry of each Ni(II) center is a distorted six-coordinate octahedron. The dihedral angle between the adjacent imidazole and thiophene ring is $2.9(2)^\circ$, and the mean deviation from the two 5-Br-TIP least-squares planes in the dinuclear complex is $0.168(2) \text{ \AA}$, also showing good planarity of the whole molecule. The whole molecule length in this case reaches 2.90 nm. Due to the above-mentioned reasons, various π - π stacking interactions and p - π stacking interactions as well as intramolecular and intermolecular hydrogen bonding interactions are observed in the packing mode of **7** (Fig. 5-7). Nevertheless, the interlayer separations between the neighboring layers are 3.364 – $3.451(2) \text{ \AA}$, which are slightly larger than those in complex **6**. This is

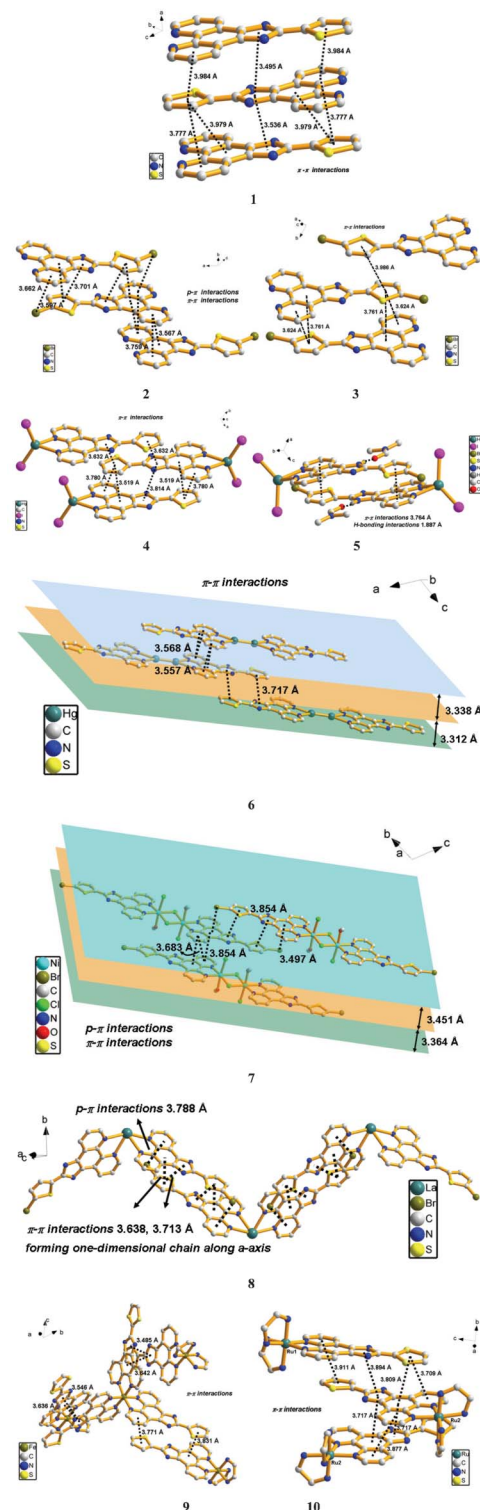


Fig. 5 Offset π - π / p - π stacking interactions in complexes **1–10** (hydrogen atoms and anions are omitted for clarity).

suggested to be the presence of apical chlorine and methanol ligands in complex **7**.

*[La(5-Br-TIP)₂(NO₃)₃](C₂H₅OH)₂ (**8**)*. An ORTEP drawing of the molecular structure of 1 : 2 mononuclear complex **8** with the atom-numbering scheme is shown in Fig. 4-8. Half a

La(III) ion, one chelating 5-Br-TIP ligand and one and a half coordinated nitrate anions as well as one free ethanol molecule are present in the asymmetric unit. The central La(III) ion is ten-coordinated by four nitrogen atoms from two chelating 5-Br-TIP ligands and six oxygen atoms from three nitrate anions, respectively. The dihedral angle between the adjacent imidazole and thiophene rings is $3.3(1)^\circ$. Several π - π stacking interactions and p - π stacking interactions are found between adjacent molecules (Fig. 5-8) forming an infinite one-dimensional (1D) supramolecular chain.

$[Fe(TIP)_3]_2(ClO_4)_4(C_2H_5OH)_2(H_2O)_5$ (**9**). The 1 : 3 mononuclear Fe(II) complex **9** with the atom-numbering scheme is shown in Fig. 4-9. It crystallizes in the triclinic space group $P\bar{1}$ and there are two Fe(II) ions, six chelating TIP ligands, four perchlorate anions, two free ethanol molecules and five free water molecules in the asymmetric unit. Two thiophene rings in six TIP ligands are refined disorderedly with different site occupancy factors. Similarly, π - π stacking interactions are observed between contiguous TIP ligands as shown in Fig. 5-9.

$[Ru(bpy)_2(TIP)]_3(PF_6)_6(CH_3OH)_2(H_2O)_{13}$ (**10**). The mononuclear Ru(II) complex **10** with the atom-numbering scheme is shown in Fig. 4-10. It crystallizes in the orthorhombic space group $I2_12_1$ and each asymmetric unit contains one and a half Ru(II) ions and TIP ligands, three bpy ligands, three hexafluorophosphate anions, one free methanol molecule and six and a half free water molecules. In this case, the 'TWIN' instruction has been used to refine the structure and an intermediate Flack value of 0.49(3) means the presence of an equal amount of δ and λ enantiomers in its solid state as we mentioned before for this family of $[Ru(bpy)_2(phen)]^{2+}$ based complexes.^{24d,30} The imidazole and thiophene rings are refined disorderedly with both 50% site occupancy factors due to the presence symmetric mirror across the Ru1 cation. The dihedral angles between the adjacent imidazole and thiophene rings in the TIP ligand are $6.2(3)^\circ$ for Ru1 and $8.8(3)^\circ$ for Ru2, respectively. The π - π stacking interactions between adjacent aromatic rings are shown in Fig. 5-10, together with the centroid-centroid distances.

Conclusion

A series of protonated salts and metal complexes of TIP and 5-Br-TIP have been synthesized and characterized in this work, where different metal/ligand molar ratios from 1 : 1 to 1 : 3 are included. Among them, dinuclear mercury(I) and nickel(II) complexes **6** and **7** exhibit excellent planarity in the lengths of 2.52 and 2.90 nm, respectively. Abundant intramolecular and intermolecular interactions, such as π - π / p - π stacking and hydrogen bonding, have been observed in their crystal packing structures. Detailed descriptions and comparisons have been made to the crystal structures, UV-Vis, 1H NMR and luminescence spectra of ligands TIP and 5-Br-TIP, protonated salts **1-3** and metal complexes **4-11**. For instance, in comparison with the TIP and 5-Br-TIP ligands, luminescence intensities for the mercury(II) and lanthanum(III) complexes **4**, **5** and **8** are found to be increased, while luminescence quenching has been detected for the nickel(II) complex **7**. In addition, large red-shifts

of 96 and 112 nm after metal-ion complexation are found in the fluorescence emission spectra of Ru(II) complexes **10** and **11**.

By checking the latest version of CCDC databases (ConQuest Version 1.14 (Build RC5), CSD Version 5.33 updated to November 2011) for ligands TIP/5-Br-TIP and their protonated salts and metal complexes, it is found that there is only one structural report on one Pb(II) complex of TIP in literature. Further work is underway on the fabrication of 1D linear semiconducting and photoresponsive nanowires by means of electropolymerization where the α -hydrogen atom of thiophene ring in TIP is oxidized and coupled with another TIP molecule forming planar bithiophene-bridged bis-imidazo[4,5-f][1,10]phenanthroline complexes $[M(TIP)_2]_n$.

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