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Luminescence, electrochemistry and host–guest properties of dinuclear platinum(II) terpyridyl complexes of sulfur-containing bridging ligands†

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A series of dinuclear platinum(II) terpyridyl and terpyridyl-crown complexes with

2,2-dicyano-1,1-ethylenedithiolate (*i*-mnt), 1,3-benzenedithiolate (SC_6H_4S -1,3) and

N,N-diethyldithiocarbamate (dtc) bridging ligands have been synthesized and characterized. Their

photophysical and electrochemical properties, together with that of the related mononuclear

platinum(II) terpyridyl-crown complex and its crown-free analogue, have been studied. The ion-binding

properties of the terpyridyl-crown complexes have been determined by electronic absorption

spectroscopy and ESI-mass spectrometry. The X-ray crystal structures of

 $[Pt(trpyC=C-benzo-15-crown-5)Cl]PF_6, [{Pt(trpy)}_2(\mu-SC_6H_4S-1,3)](PF_6)_2 and$

 $[{Pt(trpy)}_2{\mu-(i-mnt)}](PF_6)_2$ have also been determined.

Introduction

Square planar d⁸ metal complexes are well known to show a pronounced tendency to aggregate, which allows metal-metal and/or ligand-ligand interactions to occur.¹⁻⁴ Novel features in the electronic absorption and emission spectra of d⁸-d⁸ dinuclear complexes have also attracted growing attention, and have led to extensive investigations on the photophysics and photochemistry of dinuclear d^8 - d^8 metal complexes. Early works include [Rh₂(1,3diisocyanopropane)₄]²⁺, ^{1a,b} $[Rh_2(TMB)_4]^{2+}$ (TMB7nbsp;= 2,5dimethyl-2,5-diisocyanohexane),^{1b} [Rh₂(TMB)₂(dppm)₂]²⁺,^{1c} and $[Rh_2(CNR)_8]^{2+}$,^{1d} in which the lowest-lying excited state was shown to possess a relatively strong Rh-Rh bond. The photophysical properties of dinuclear platinum(II) complexes have also been studied. The most thoroughly investigated systems include the infinite-chain [Pt(CN)₄]^{2-2b} and the luminescent dinuclear complexes such as $[Pt_2(H_2P_2O_5)_4]^{4-2c}$ that possess metal-metal bonded $(d_{\sigma^*})^1(p_{\sigma})^1$ excited states; the absorption and emission properties of which have been studied by Gray, Roundhill and Che in detail.^{2c} Recently, there has also been a growing interest in the study of platinum(II) polypyridine complexes owing to the intriguing photophysical and spectroscopic properties reported of this class compounds,³⁻⁷ in particular platinum(II) terpyridyl systems,⁴⁻⁷ in which metal-metal and/or ligand-ligand interactions have been shown to play an important role in governing the spectroscopic properties of these complexes. Extension of the work to dinuclear systems with well-defined metal-metal separation has also been made. Examples include the studies of $[{Pt(trpy)}_2(\mu$ gua)]³⁺ (gua = guandine anion)^{5b} and $[{Pt(trpy)}_2(\mu-X)]^{3+}$ (X = pyrazole, azaindole, canavanine, diphenylformamidine),5a,c,d which provided insights into the role of platinum-platinum separation in governing the spectroscopic properties of these complexes. Apart

from the nitrogen-donor bridging ligands, other related dinuclear platinum(II) terpyridyl systems using sulfur-containing bridging ligands, such as $[{Pt(trpy)}_2(\mu-dtc)]^{3+}$, ^{5e} and $[{Pt(trpy)}_2(\mu-dtc)]^{3+}$, ^{5e} DMcT]^{2+5f} (dtc = N,N-diethyldithiocarbamate and DMcT = 2,5-dimercapto-1,3,4-thiadiazole), were also reported. Despite a number of studies on these platinum(II) terpyridyl systems,4-7 relatively less was explored of the utilization of these systems for chemosensing studies.^{6,7a,b,f-m} The recent growth of interests in the chemistry of crown ethers and other related inclusion compounds has been prompted in part by the potentials of utilizing such compounds in molecular recognition studies and the design of molecular switches and probes. There are numerous excellent reviews on transition metal complexes as ion and molecular sensors,8 however, utilization of crown ether in dinuclear systems is rare. Recently, we reported a series of novel crown ether-containing dinuclear gold(I) complexes, which showed interesting luminescence properties upon binding of potassium and caesium ions.9 As an extension of our reported mononuclear crown ether-containing platinum(II) terpyridyl complexes, [Pt(trpy)(S-benzo-15-crown-5)]⁺,^{6a} [Pt(trpy)(C=C-benzo-15-crown-5)]⁺,^{7a,j} and [Pt(trpy)(C=C-N-phenylaza-15-crown-5)]⁺,^{7j} attempts have been made to design and synthesize dinuclear d⁸-d⁸ platinum(II) terpyridyl and terpyridyl-crown complexes containing various sulfur-containing bridging ligands and to investigate the effect of metal-metal interaction on the luminescence properties of these dinuclear platinum(II) terpyridyl system. Exploration into the possibility of utilizing these dinuclear crown ether-containing platinum(II) complexes with metal-metal interactions for chemosensing work has been made. Herein are reported the syntheses, photophysics, electrochemistry and supramolecular ion-binding properties of a series of dinuclear platinum(II) terpyridyl and terpyridyl-crown complexes with 2,2-dicyano-1,1-ethylenedithiolate (i-mnt), 1,3benzenedithiolate (SC₆H₄S-1,3) and N,N-diethyldithiocarbamate (dtc) bridging ligands. The syntheses and photophysical behaviour of the related mononuclear platinum(II) terpyridylcrown complex and its crown-free analogue have also been studied.

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Experimental

Reagents and materials

Dichloro(1,5-cyclooctadiene)platinum(II) and 2,2':6',2"-terpyridine were obtained from Strem Chemicals Inc. 1,3-Benzenedithiol ((HS)₂C₆H₄-1,3) was purchased from Aldrich Chemical Co. [Pt(trpy)Cl]Cl·2H₂O,¹⁰ trpyC=C-benzo-15-crown-5,¹¹ trpy-C=CC₆H₃(OCH₃)₂-3,4,¹¹ potassium 2,2-dicyano-1,1-ethylenedithiolate (K₂(*i*-mnt)),¹² diethylammonium 2,2-dicyano-1,1-ethylenedithiolate ((Et₂NH₂)₂(*i*-mnt)),¹² and diethylammonium *N*,*N*-diethyldithiocarbamate ((Et₂NH₂)dtc)¹² were synthesized according to the published procedures. Tetra-*n*-butylammonium hexafluorophosphate ("Bu₄NPF₆) (Aldrich, 98%) were purchased and was recrystallized three times from hot ethanol prior to use. Triethylamine was distilled over potassium hydroxide and stored in the presence of potassium hydroxide prior to use. All other reagents were of analytical grade and were used as received.

Synthesis of platinum(II) terpyridyl precursors

 $[Pt(trpyC=C-benzo-15-crown-5)Cl]X (X = Cl 1a; PF_6 1b).$ To a suspension of Pt(COD)Cl₂ (100 mg, 0.27 mmol) in water-methanol (1:1 v/v)(30 mL) was added trpyC=C-benzo-15-crown-5(153 mg, 0.29 mmol). The reaction mixture was stirred at 50 °C for 1 h during which the orange solution turned to a deep red solution. After evaporation to dryness, red solids of 1a were obtained and recrystallized by diffusion of diethyl ether vapour into an acetonitrile solution of the complex. On the other hand, diffraction quality crystals of 1b were collected after metathesis reaction with tetra-n-butylammonium hexafluorophosphate in methanol, followed by subsequent recrystallization by diffusion of diethyl ether vapour into an acetonitrile solution of the product to give 1b as red crystals. Yield for 1b: 128 mg, 53%. ¹H NMR (400 MHz, $(CD_3)_2$ SO, 298 K, relative to Me₄Si): δ 3.64 (m, 8H, -OCH₂-), 3.81 (m, 4H, C₆H₃OCH₂-), 4.13 (m, 4H, C₆H₃OCH₂-), 7.09 (d, 1H, J = 8.3 Hz, $-C_6H_3-$), 7.19 (d, 1H, J = 1.7 Hz, $-C_6H_3-$), 7.28 (dd, 1H, J = 1.7 Hz, 8.3 Hz, $-C_6H_{3-}$), 7.95 (t, 2H, J = 6.2 Hz, trpy), 8.51 (t, 2H, J = 7.7 Hz, trpy), 8.68 (d, 2H, J = 7.7 Hz, trpy), 8.82 (s, 2H, trpy), 8.87 (d, 2H, J = 4.8 Hz, trpy). IR (Nujol mull on KBr disc, v/cm^{-1}): 2120 v(C=C). Positive ESI-MS: m/z754 $[M - PF_6]^+$, 1653 $[2M - PF_6]^+$. Anal. calcd for $C_{31}H_{29}N_3O_5$ -PtClPF₆: C 41.43, H 3.22, N 4.68. Found: C 41.48, H 3.26, N 4.70.

[Pt(trpyC≡CC₆H₃(OCH₃)₂-3,4)Cl]X (X = Cl 2a; PF₆ 2b). The procedure was similar to that for complex 1 except trpyC≡CC₆H₃(OCH₃)₂-3,4 (114 mg, 0.29 mmol) was used in place of trpyC≡C-benzo-15-crown-5 to give red crystals of **2a** and **2b**. Yield for **2b**: 163 mg, 59%. ¹H NMR (400 MHz, (CD₃)₂SO, 298 K, relative to Me₄Si): δ 3.88 (s, 3H, –OCH₃), 3.90 (s, 3H, –OCH₃), 7.04 (d, 1H, J = 8.4 Hz, –C₆H₃–), 7.20 (d, 1H, J = 2.0 Hz, –C₆H₃–), 7.31 (dd, 1H, J = 2.0 Hz, 8.4 Hz, –C₆H₃–), 7.95 (t, 2H, J = 7.1 Hz, trpy), 8.55 (t, 2H, J = 7.1 Hz, trpy), 8.69 (d, 2H, J = 8.0 Hz, trpy), 8.80 (s, 2H, trpy), 8.92 (d, 2H, J = 4.6 Hz, trpy). IR (Nujol mull on KBr disc, ν/cm^{-1}): 2122 ν (C≡C). Positive ESI-MS: m/z 623 [M – PF₆]⁺, 1391 [2M – PF₆]⁺. Anal. calcd for C₂₅H₁₉N₃O₂-PtClPF₆: C 39.06, H 2.47, N 5.47. Found: C 39.01, H 2.43, N 5.49.

Synthesis of dinuclear platinum(II) terpyridyl complexes

 $\{ Pt(trpy) \}_2(\mu - SC_6H_4S - 1, 3) \} (PF_6)_2 (3).$ To a stirred solution of [Pt(trpy)Cl]Cl·H₂O (375 mg, 0.70 mmol) in methanol (40 mL) was added 1,3-benzenedithiol (50 mg, 0.35 mmol) in the presence of an excess of triethylamine (0.1 mL). The reaction mixture turned from red to dark purple immediately and was stirred for 4 h at room temperature. The resultant mixture was filtered and to the filtrate was added a saturated solution of tetra-n-butylammonium hexafluorophosphate in methanol. The product precipitated out and was filtered, washed with methanol and air dried. Subsequent recrystallization by diffusion of diethyl ether vapour into an acetonitrile solution of the product gave 3 as dark purple crystals. Yield: 1.35 g, 75%. ¹H NMR (400 MHz, CD₃CN, 298 K, relative to Me₄Si): δ 6.91 (t, 1H, J = 7.8 Hz, $-C_6H_4$ -), 7.21 (dd, 2H, J = 1.9 Hz, 7.8 Hz, $-C_6H_{4-}$), 7.58 (m, 4H, trpy), 8.10 (m, 8H, trpy), 8.21 (d, 4H, J = 8.1 Hz, trpy), 8.41 (s, 1H, $-C_6H_4-$), 8.49 (t, 2H, J = 8.1 Hz, trpy), 9.11 (d, 4H, J = 5.6 Hz, trpy). Positive ESI-MS: m/z 1141 $[M - PF_6]^+$, 498 $[M - 2PF_6]^{2+}$. Anal. calcd for C₃₆H₂₆N₆Pt₂S₂P₂F₁₂: C 33.59, H 2.02, N 6.53. Found: C 33.61, H 1.99, N 6.57.

 $[{Pt(trpy)}_{2}(\mu-(i-mnt))](PF_{6})_{2}$ (4). To a stirred solution of [Pt(trpy)Cl]Cl·H₂O (100 mg, 0.19 mmol) in water (30 mL) was added K₂(*i*-mnt) (22 mg, 0.09 mmol) in water (10 mL) in a dropwise manner. The orange solution turned to a dark red solution immediately and was stirred for 2 h at room temperature. The resultant mixture was filtered and to the filtrate was added a saturated solution of tetra-n-butylammonium hexafluorophosphate in methanol. The product was isolated, washed with methanol and air dried. Subsequent recrystallization by diffusion of diethyl ether vapour into an acetonitrile solution of the product gave 4 as dark red crystals. Yield: 400 mg, 82%. ¹H NMR (400 MHz, CD₃CN, 298 K, relative to Me₄Si): δ 7.57 (t, 4H, J = 7.7 Hz, trpy), 7.85 (d, 4H, J = 8.0 Hz, trpy), 7.92 (d, 4H, J = 8.2 Hz, trpy), 8.24 (t, 4H, J = 7.7 Hz, trpy), 8.37 (t, 2H, J = 8.0 Hz, trpy), 8.47 (d, 4H, J = 5.4 Hz, trpy). IR (Nujol mull on KBr disc, v/cm^{-1}): 1446 v(C=C). Positive ESI-MS: m/z 1141 [M – PF₆]⁺, 498 [M – 2PF₆]²⁺. Anal. calcd for C₃₄H₂₂N₈Pt₂S₂P₂F₁₂: C 31.72, H 1.71, N 8.71. Found: C 31.73, H 1.75, N 8.76.

 $[{Pt(trpyC=C-benzo-15-crown-5)}_{2}{\mu-(i-mnt)}](PF_{6})_{2}$ (5). The procedure was similar to that for complex 4 except [Pt(trpyC=C-benzo-15-crown-5)Cl]Cl (1a) (100 mg, 0.13 mmol) and (Et₂NH₂)₂(*i*-mnt) (18 mg, 0.06 mmol) were used in place of $[Pt(trpy)Cl]Cl \cdot H_2O$ and $K_2(i-mnt)$, respectively, to give dark red crystals of 5. Yield: 325 mg, 67%. ¹H NMR (400 MHz, (CD₃)₂SO, 298 K, relative to Me₄Si): δ 3.67 (m, 16H, -OCH₂-), 3.86 (m, 12H, -OCH₂-, C₆H₃OCH₂-), 4.15 (m, 4H, C₆H₃OCH₂-), 6.96 (d, 2H, J = 8.2 Hz, $-C_6H_3$ -), 7.00 (d, 2H, J = 1.3 Hz, $-C_6H_3$ -), 7.19 $(dd, 2H, J = 1.3 Hz, 8.2 Hz, -C_6H_3-), 7.81 (m, 4H, trpy), 8.41 (m, 4H, trpy), 8.41$ 8H, trpy), 8.60 (d, 4H, J = 5.3 Hz, trpy), 8.63 (s, 4H, trpy). IR (Nujol mull on KBr disc, v/cm^{-1}): 2201 v(C=C), 1450 v(C=C). Positive ESI-MS: m/z 1722 $[M - PF_6]^+$, 789 $[2M - 2PF_6]^{2+}$. Anal. calcd for C₆₆H₅₈N₈O₁₀Pt₂S₂P₂F₁₂: C 42.44, H 3.11, N 6.00. Found: C 42.47, H 3.08, N 5.95.

 $[{Pt(trpyC=CC_6H_3(OCH_3)_2-3,4)}_2{\mu-(i-mnt)}](PF_6)_2 (6).$ The procedure was similar to that for complex 5 except [Pt(trpyC=CC_6H_3(OCH_3)_2-3,4)Cl]Cl (2a) (86 mg, 0.13 mmol) was used in place of [Pt(trpyC=C-benzo-15-crown-5)Cl]Cl to give dark

red crystals of **6**. Yield: 259 mg, 62%. ¹H NMR (400 MHz, $(CD_3)_2SO$, 298 K, relative to Me₄Si): δ 3.68 (s, 6H, $-OCH_3$), 3.85 (s, 6H, $-OCH_3$), 6.96 (d, 2H, J = 8.4 Hz, $-C_6H_3-$), 7.00 (d, 2H, J = 1.4 Hz, $-C_6H_3-$), 7.17 (dd, 2H, J = 1.4 Hz, 8.4 Hz, $-C_6H_3-$), 7.78 (m, 4H, trpy), 8.39 (m, 8H, trpy), 8.59 (d, 4H, J = 5.4 Hz, trpy), 8.62 (s, 4H, trpy). IR (Nujol mull on KBr disc, ν/cm^{-1}): 2204 $\nu(C=C)$, 1451 $\nu(C=C)$. Positive ESI-MS: m/z 1461 [M – PF₆]⁺, 658 [M – 2PF₆]²⁺. Anal. calcd for C₅₄H₃₈N₈O₄Pt₂S₂P₂F₁₂: C 40.35, H 2.37, N 6.97. Found: C 40.37, H 2.38, N 6.94.

 $\{ Pt(trpyC \equiv C-benzo-15-crown-5) \}_2(\mu-dtc) | (PF_6)_3(7). The pro$ cedure was similar to that for complex 4 except [Pt(trpyC=Cbenzo-15-crown-5)Cl]Cl (1a) (100 mg, 0.13 mmol) and (Et₂NH₂)dtc (14 mg, 0.06 mmol) were used in place of $[Pt(trpy)Cl]Cl \cdot H_2O$ and $K_2(i-mnt)$, respectively, to give dark red crystals of 7. Yield: 331 mg, 63%. ¹H NMR (400 MHz, CD₃CN, 298 K, relative to Me₄Si): δ 1.61 (t, 3H, J = 7.2 Hz, $-CH_2CH_3$), 3.67 (m, 24H, -OCH₂-), 3.85 (m, 4H, C₆H₃OCH₂-), 4.06 (m, 4H, $C_6H_3OCH_2$ -), 4.28 (q, 2H, J = 7.2 Hz, $-CH_2CH_3$), 6.59 (d, 2H, J = 8.2 Hz, $-C_6H_3$ -), 6.71 (d, 2H, J = 1.6 Hz, $-C_6H_3$ -), 6.79 (dd, 2H, J = 1.6 Hz, 8.2 Hz, $-C_6H_3$ -), 7.65 (t, 2H, J = 6.3 Hz, trpy), 7.84 (d, 2H, J = 7.9 Hz, trpy), 7.92 (s, 2H, trpy), 8.25 (t, 2H, J = 7.9 Hz, trpy), 8.52 (d, 2H, J = 4.9 Hz, trpy). IR (Nujol mull on KBr disc, v/cm^{-1}): 2196 v(C=C). Positive ESI-MS: m/z867 $[M - Pt(trpyC = C-benzo-15-crown-5) - 3PF_6]^+$. Anal. calcd for C₆₇H₆₈N₇O₁₀Pt₂S₂P₃F₁₈: C 39.82, H 3.37, N 4.85. Found: C 39.80, H 3.33, N 4.81.

 $[{Pt(trpyC=CC_{6}H_{3}(OCH_{3})_{2}-3,4)}_{2}(\mu-dtc)](PF_{6})_{3}$ (8). The procedure was similar to that for complex 5 except $[Pt(trpyC=CC_6H_3(OCH_3)_2-3,4)Cl]Cl$ (2a) (85 mg, 0.13 mmol) was used in place of [Pt(trpyC=C-benzo-15-crown-5)Cl]Cl to give dark red crystals of 8. Yield: 274 mg, 60%. ¹H NMR (400 MHz, CD₃CN, 298 K, relative to Me₄Si): δ 1.62 (t, 3H, J = 7.1 Hz, -CH₂CH₃), 3.69 (s, 6H, -OCH₃), 3.90 (s, 6H, -OCH₃), 4.29 (q, 2H, J = 7.1 Hz, $-CH_2CH_3$), 6.87 (d, 2H, J = 8.2 Hz, $-C_6H_3$ -), 7.00 (d, 2H, J = 1.6 Hz, $-C_6H_3$ -), 7.13 (dd, 2H, J =1.6 Hz, 8.2 Hz, $-C_6H_3$ -), 7.66 (t, 4H, J = 6.7 Hz, trpy), 7.95 (d, 4H, J = 7.9 Hz, trpy), 8.08 (s, 4H, trpy), 8.30 (t, 4H, J =7.9 Hz, trpy), 8.60 (d, 4H, J = 5.7 Hz, trpy). IR (Nujol mull on KBr disc, v/cm^{-1}): 2190 v(C=C). Positive ESI-MS: m/z 736 $[M - Pt(trpyC=CC_6H_3(OCH_3)_2-3,4) - 3PF_6]^+$. Anal. calcd for C₅₅H₄₈N₇O₄Pt₂S₂P₃F₁₈: C 37.52, H 2.73, N 5.57. Found: C 37.50, H 2.75, N 5.53.

Physical measurements and instrumentation

UV-vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, IR spectra on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000–400 cm⁻¹), and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorometer. Solid-state photophysical studies were carried out with solid samples contained in a quartz tube inside a quartz-walled Dewar flask. Measurements of the butyronitrile glasses or solid-state samples at 77 K were similarly conducted with liquid nitrogen filled in the optical Dewar flask. Excited state lifetimes were measured using a conventional laser system. The excitation source was the 355-nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd-YAG laser (10 Hz). All solutions for photophysical studies were degassed on a high-vacuum line in a two-compartment cell consisting of a 10-ml Pyrex bulb and a 1-cm path length quartz cuvette and sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were subject to no less than four freeze–pump–thaw cycles.

¹H NMR (400 MHz) spectra were recorded on a Bruker DPX-400 FT-NMR spectrometer at 298 K and chemical shifts are reported relative to Me₄Si. Positive ESI mass spectra were recorded on a Finnigan LCQ mass spectrometer. Elemental analyses of the new complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences. Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. model CHI 620 Electrochemical Analyzer, which was interfaced to a personal computer. The electrolytic cell used was a conventional two-compartment cell. Electrochemical measurements were performed in acetonitrile solutions with 0.1 M "Bu₄NPF₆ (TBAH) as supporting electrolyte at room temperature. The reference electrode was a Ag/AgNO₃ (0.1 M in acetonitrile) electrode and the working electrode was a glassy carbon (Atomergic Chemetal V25) electrode with a piece of platinum wire as counter electrode in a compartment which is separated from the working electrode by a sintered glass frit. The ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference.13a All solutions for electrochemical studies were deaerated with pre-purified argon gas just before measurements. Treatment of the electrode surfaces was as reported previously.13b

The electronic absorption spectral titration for binding constant determination was performed with a Hewlett-Packard 8452A diode array spectrophotometer at 25 °C, which was controlled by a Lauda RM6 compact low-temperature thermostat. Supporting electrolyte (0.1 mol dm^{-3 n}Bu₄NPF₆) was added to maintain a constant ionic strength of the sample solution in order to avoid any changes arising from a change in the ionic strength of the medium. Binding constants for 1 : 1 complexation were determined by non-linear least-squares fits to eqn (1), in which the derivations were described previously.¹⁴

$$X = X_{0} + \frac{X_{\lim} - X_{0}}{2[\operatorname{Pt}]_{\mathrm{T}}} \left\{ [\operatorname{Pt}]_{\mathrm{T}} + [\operatorname{M}^{n^{+}}] + \frac{1}{K_{S}} - \left[\left([\operatorname{Pt}]_{\mathrm{T}} + [\operatorname{M}^{n^{+}}] + \frac{1}{K_{S}} \right)^{2} - 4 [\operatorname{Pt}]_{\mathrm{T}} [\operatorname{M}^{n^{+}}] \right]^{\frac{1}{2}} \right\}$$
(1)

where X_0 and X are the absorbance of complex at a selected wavelength in the absence and presence of the metal cation, respectively, $[Pt]_T$ is the total concentration of the complex, $[M^{n+}]$ is the concentration of the metal cation M^{n+} , X_{iim} is the limiting value of absorbance in the presence of excess metal ion and K_s is the stability constant.

Crystal structure determination

Single-crystals of $[Pt(trpyC=C-benzo-15-crown-5)Cl]PF_6$ (1b), $[{Pt(trpy)}_2(\mu-SC_6H_4S-1,3)](PF_6)_2$ (3) and $[{Pt(trpy)}_2{\mu-(i-mnt)}](PF_6)_2$ (4) suitable for X-ray diffraction studies were grown by vapour diffusion of diethyl ether into an acetonitrile solution of the respective complexes. All the experimental details are given in Table 1.

	1b	3	4-4CH ₃ CN
Empirical formula	$[C_{31}H_{29}ClN_3O_5PF_6Pt]$	$[C_{36}H_{26}N_6S_2P_2F_{12}Pt_2]$	$[(C_{34}H_{22}N_8S_2P_2F_{12}Pt_2)\cdot 4CH_3CN]$
Formula Weight	899.08	1286.87	1451.04
T/K	301(2)	301	301
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	<i>P</i> 1̄ (no. 2)	$P2_1/c$ (no. 2)
Unit cell dimensions	$a = 6.2690(13) \text{ Å } \alpha = 90^{\circ}$	$a = 8.5245(9) \text{ Å } \alpha = 105.638(7)^{\circ}$	$a = 13.784(3) \text{ Å } \alpha = 90^{\circ}$
	$b = 14.713(3) \text{ Å } \beta = 95.08(3)^{\circ}$	$b = 13.522(2) \text{ Å } \beta = 95.371(7)^{\circ}$	$b = 22.003(2) \text{ Å } \beta = 108.09(1)^{\circ}$
	$c = 34.398(7) \text{ Å } \gamma = 90^{\circ}$	$c = 17.921(1) \text{ Å } \gamma = 96.149(7)^{\circ}$	$c = 17.103(2) \text{ Å } \gamma = 90^{\circ}$
$V/Å^3$	3160.3(11)	1961.3(3)	4930(1)
Crystal colour	Orange	Purple	Red
Z	4	2	8
F(000)	1760	1220	2784
Calculated density/g cm ⁻³	1.890	2.179	1.955
Crystal size/mm ³	$0.30 \times 0.15 \times 0.05$	$0.40 \times 0.15 \times 0.07$	$0.30 \times 0.10 \times 0.07$
λ/Å	0.71073	0.71073	0.71073
μ/mm^{-1}	4.657	7.380	5.887
$2\theta_{\rm max}/^{\circ}$	50.84	50	50
Index range	$-7 \le h \le 6$	$-10 \le h \le 10$	$0 \le h \le 16$
	$-10 \le k \le 17$	$0 \le k \le 16$	$0 \le k \le 26$
	$-39 \le l \le 39$	$-21 \le l \le 20$	$-20 \le l \le 19$
Total number of reflections	7114	7208	9320
Unique reflections	$3657 [R_{int} = 0.0523]$	$6888 [R_{int} = 0.0280]$	$8927 [R_{int} = 0.0329]$
No. of data used in refinement	3657	5288	6013
Completeness (%)	62.6	99.7	99.8
No. of parameters refined	433	541	639
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.913	1.21	1.58
Final <i>R</i> indices	$R_1 = 0.0376, wR_2 = 0.0860^a$	$R = 0.024, wR = 0.033^{b}$	$R = 0.034, WR = 0.041^{b}$
Largest diffraction peak and hole	0.542 and -0.822 e Å ⁻³	$0.82, 0.58 \text{ e} \text{\AA}^{-3}$	1.50, 1.10 e Å ⁻³
a w = 1/[$\sigma^{2}(F_{0}^{2})$ +(0.054 <i>P</i>) ²], where <i>P</i>	P is $[2F_c^2 + Max(F_c^2, 0)]/3$ with $I > 2\sigma(I)$). ${}^{b} W = 4F_{0}{}^{2}/\sigma^{2}(F_{0}{}^{2})$, where $\sigma^{2}(F_{0}{}^{2}) = [$	$[\sigma^2(I) + (0.02F_0^2)^2]$ with $I > 3\sigma(I)$.

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A crystal of 1b mounted on a glass fibre was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized MoKa radiation $(\lambda = 0.71073 \text{ Å})$. The images were interpreted and intensities integrated using the program DENZO.15 The structure was solved by direct methods employing SHELXS-9716 program on a PC. The Pt, Cl and many non-H atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-9717 on a PC. One crystallographic asymmetric unit consisted of one formula unit, including one PF₆ anion. In the final stage of least-squares refinement, all atoms were refined anisotropically. H atoms were generated by program SHELXL-97.17 The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices.

Crystals of **3** and **4** mounted in a glass capillary were used for data collection at 28 °C on a Rigaku AFC7R diffractometer with graphite monochromatized MoK α radiation ($\lambda = 0.71073$ Å) using ω -2 θ scans with ω -scan angle (0.73 + 0.35 tan θ)° at a scan speed of 8.0° min⁻¹ (up to 6 scans for reflection with $I < 15\sigma(I)$). The space group was determined based on a statistical analysis of intensity distribution and the successful refinement of the structure solved by Patterson methods and expanded by Fourier methods (PATTY)¹⁸ and refinement by full-matrix least squares using the software package TeXsan¹⁹ on a Silicon Graphics Indy computer. The crystallographic asymmetric unit of **3** consisted of one formula unit. In the least-squares refinement, all 60 non-H atoms were refined anisotropically and 26 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. For **4**, one crystallographic asymmetric unit consisted of one formula unit. The F atoms of one of the anion were disordered and were placed at 11 positions with F(7), F(7'), F(8), F(8'), F(9), F(10), F(10'), F(11), F(11'), F(12) and F(12') having occupation numbers of 0.8, 0.4, 0.4, 0.4, 0.8, 0.7, 0.5, 0.6, 0.4, 0.7 and 0.3, respectively. In the least-squares refinement, 66 non-H atoms were refined anisotropically, the 11 disordered F atoms with thermal parameters equal to 1.3 times that of the attached C atoms were not refined.

Results and discussion

Syntheses

[Pt(trpyC≡C-benzo-15-crown-5)Cl]Cl (1a) and [Pt(trpyC≡ CC₆H₃(OCH₃)₂-3,4)Cl]Cl (2a), which were prepared by the modification of the literature reported procedures for [Pt(trpy)Cl]Cl·H₂O,¹³ together with [Pt(trpy)Cl]Cl·H₂O, were found to be good starting materials for the syntheses of the dinuclear platinum(II) terpyridyl complexes. Reaction of [Pt(trpy)Cl]Cl·H₂O with 1,3-benzenedithiol in a 2 : 1 molar ratio in methanol in the presence of triethylamine as the base afforded **3** as dark purple crystals. **4** was isolated as dark red crystals by the reaction of [Pt(trpy)Cl]Cl·H₂O with K₂(*i*-mnt) in a 2 : 1



molar ratio in water. The thiolate-bridged dinuclear platinum(II) crown-ether containing terpyridyl complexes, 5 and 7, were synthesized by the reaction of [Pt(trpyC≡C-benzo-15-crown-5)Cl]Cl with the corresponding salts of *i*-mnt and dtc in water at room temperature, respectively. The diethylammonium salt of *i*-mnt was used for the synthesis of 5 instead of $K_2(i$ -mnt) as in the preparation of 4 to avoid the presence of K^+ ions, which are believed to bind to the crown moieties. Their crown-free analogues 6 and 8 were also successfully synthesized and characterized in a similar manner. The schematic drawings of the newly synthesized mononuclear precursor complexes and the dinuclear platinum(II) terpyridyl and terpyridyl-crown complexes are depicted in Scheme 1. The identities of all the newly synthesized dinuclear platinum(II) complexes and platinum(II) precursor complexes have been confirmed by satisfactory elemental analyses, ¹H HMR spectroscopy, IR spectroscopy, and ESI-mass spectrometry. The crystal structures of [Pt(trpyC=C-benzo-15crown-5)Cl]PF₆ (1b), $[{Pt(trpy)}_2(\mu-SC_6H_4S-1,3)](PF_6)_2$ (3) and $[{Pt(trpy)}_2{\mu-(i-mnt)}](PF_6)_2$ (4) have also been determined.

X-Ray crystal structure determination

Fig. 1–3 show the perspective drawings of the complex cation of $[Pt(trpyC=C-benzo-15-crown-5)Cl]PF_6$ (1b), $[{Pt(trpy)}_2(\mu-SC_6H_4S-1,3)](PF_6)_2$ (3) and $[{Pt(trpy)}_2{\mu-(i-mnt)}](PF_6)_2$ (4), respectively. The crystal structure determination data are given in Table 1 while the selected bond distances and bond angles are listed in Table 2. The coordination geometry of all the complexes at the platinum centre is distorted square planar, in which the distance of the platinum to the inner nitrogen atom of the terpyridine ligand is significantly shorter than those of the other two outer nitrogen atoms. All the Pt–N distances and N–Pt–N bond angles are comparable to those obtained in typical platinum(II) terpyridyl complexes.^{4a-e,5,6,7a-f,h,i,k} The Pt–Cl distance of 2.308 Å in **1b** is



Fig. 1 Perspective drawing of the complex cation of $[Pt(trpyC=C-benzo-15-crown-5)Cl]PF_6$ 1b with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 40% probability level.

comparable to that of 2.302 Å in the related [Pt(trpy)Cl]ClO₄.^{5b} The C(trpy)–C=C unit is essentially linear with C(8)–C(16)–C(17) bond angle of 177.4° and C(16)–C(17)–C(18) bond angle of 177.4° While the C=C bond length of 1.173 Å is typical of alkynes. The phenyl ring of B15C-5 is essentially co-planar with respect to the [Pt(trpy)] plane with the interplanar angle of 3.218°, suggesting that delocalization within the trpyC=C-benzo-15-crown-5 ligand. Neither short Pt ··· Pt contacts (the shortest Pt ··· Pt distance = 5.022 Å) nor significant π – π interactions were observed in the crystal lattices of **1b**.

In complex **3**, the bridging ligand, $-SC_6H_4S_-$, links the two platinum(II)-terpyridine co-ordination planes in an *anti*-configuration with Pt(1)–S(1)–C(16) and Pt(2)–S(2)–C(20) bond angles of 100.7° and 107.4°, respectively, and a dihedral angle of 36.5° between the two coordination planes (Fig. 2). The bond lengths of the Pt–S [Pt(1)–S(1), 2.316 Å; Pt(2)–S(2), 2.303 Å] and S–C [S(1)–C(16), 1.781 Å; S(1)–C(20), 1.774 Å] bonds are



Fig. 2 Perspective drawing of the complex cation of $[\{Pt(trpy)\}_2(\mu-SC_6H_4S-1,3)](PF_6)_2$ **3** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 40% probability level.

comparable to that previously reported for platinum(II) terpyridyl^{3h} and diimine²⁰ complexes containing aromatic thiolate ligands. Due to its *anti*-conformation, the two platinum(II)-terpyridyl planes are directed away each other and no intramolecular metal-metal or ligand-ligand interactions are observed. It is interesting to note that the molecules exist in a dimeric structure with one short and one long Pt…Pt distance of 3.753 Å and 4.375 Å, respectively, between adjacent dinuclear molecules on different sides of the Pt(trpy) moieties (Fig. 3). Such short Pt…Pt contacts together with the interplanar angle and distance of 0.0° and 3.5725 Å, respectively, may suggest the possible existence of some weak intermolecular Pt…Pt and π - π interactions between the platinum-terpyridine moieties.

Fig. 4(a) shows the perspective drawing of the complex cation of **4**, in which two platinum(II)-terpyridyl moieties are connected by the *i*-mnt bridging ligand to form a molecular clip-like structure. The two platinum-terpyridine co-ordination planes of complex **4** are arranged in a *syn*-configuration with the interplanar

Table 2 Selected bond distances (Å) and bond angles (°) with estimated standard deviations (esds) in parentheses for 1b, 3 and 4

1b			
Pt(1)-N(1)	2.01(1)	Pt(1)-Cl(1)	2.31(1)
Pt(1)-N(2)	1.97(1)	C(16)–C(17)	1.17(1)
Pt(1) - N(3)	2.03(1)	C(8)–C(16)	1.43(1)
C(17)–C(18)	1.44(1)		
N(1)-Pt(1)-N(2)	81.8(4)	N(3)-Pt(1)-Cl(1)	99.8(2)
N(2)-Pt(1)-N(3)	80.7(4)	C(8)-C(16)-C(17)	178.4(13)
N(1)-Pt(1)-N(3)	162.4(3)	C(16)-C(17)-C(18)	177.4(13)
N(1)-Pt(1)-Cl(1)	97.8(2)	C(17)-C(18)-C(19)	119.1(9)
N(2)-Pt(1)-Cl(1)	179.6(3)	C(17)-C(18)-C(23)	121.5(10)
3			
Pt(1)-S(1)	2.316(1)	Pt(1)-N(3)	2.032(4)
Pt(2)–S(2)	2.303(2)	Pt(2)-N(4)	2.024(5)
Pt(1)–N(1)	2.034(4)	Pt(2) - N(5)	1.964(4)
Pt(1)–N(2)	1.965(4)	Pt(2)–N(6)	2.021(5)
N(1)-Pt(1)-N(2)	80.8(2)	N(2)-Pt(1)-S(1)	178.6(1)
N(2)-Pt(1)-N(3)	80.8(2)	N(3)-Pt(1)-S(1)	100.3(1)
N(1)-Pt(1)-N(3)	161.5(2)	N(4)-Pt(2)-S(2)	101.3(1)
N(4)-Pt(2)-N(5)	80.8(2)	N(5)-Pt(2)-S(2)	177.5(1)
N(5)-Pt(2)-N(6)	80.3(2)	N(6)-Pt(2)-S(2)	97.5(1)
N(4)-Pt(2)-N(6)	161.1(2)	Pt(1)-S(1)-C(16)	100.7(2)
N(1)-Pt(1)-S(1)	98.1(1)	Pt(2)-S(2)-C(20)	107.4(2)
4			
Pt(1)-S(1)	2.297(2)	Pt(2)-N(4)	2.035(7)
Pt(2)-S(2)	2.314(2)	Pt(2)-N(5)	1.957(7)
Pt(1)-N(1)	2.034(6)	Pt(2)-N(6)	2.033(7)
Pt(1)-N(2)	1.955(6)	Pt(1)-Pt(2)	3.0882(8)
Pt(1) - N(3)	2.031(6)		
N(1)-Pt(1)-N(2)	80.6(3)	N(5)-Pt(2)-S(2)	178.5(2)
N(2)-Pt(1)-N(3)	80.7(3)	N(6)-Pt(2)-S(2)	98.5(2)
N(1)-Pt(1)-N(3)	161.1(3)	Pt(1)-S(1)-C(1)	109.4(3)
N(4)-Pt(2)-N(5)	80.9(3)	Pt(2)-S(2)-C(1)	109.8(2)
N(5)-Pt(2)-N(6)	80.1(3)	Pt(2)-Pt(1)-N(1)	89.4(2)
N(4)-Pt(2)-N(6)	161.0(3)	Pt(2)-Pt(1)-N(2)	100.8(2)
N(1)-Pt(1)-S(1)	97.6(2)	Pt(2)-Pt(1)-N(3)	96.7(2)
N(2)-Pt(1)-S(1)	175.8(2)	Pt(2)-Pt(1)-N(4)	96.3(2)
N(3)-Pt(1)-S(1)	100.9(2)	Pt(2)-Pt(1)-N(5)	95.1(2)
N(4)-Pt(2)-S(2)	100.4(2)	Pt(2)-Pt(1)-N(6)	86.3(2)

angle and distance of 12.290° and 3.354 Å. The intramolecular Pt(1) · · · Pt(2) distance of 3.088 Å is comparable to those found in [{Pt(trpy)}₂(µ-gua)](ClO₄)₃ [3.09 and 3.07 Å],^{5b} [{Pt(trpy)}₂(µ-dtc)](PF₆)₃ [3.052 Å],^{5e} and [{Pt(trpy)}₂(µ-NHC(=O)Me)](OTf)₃ [3.119 Å].^{5g} The Pt–S [Pt(1)–S(1), 2.298 Å; Pt(2)–S(2), 2.314 Å] and S–C [S(1)–C(1), 1.733 Å; S(2)–C(1), 1.734 Å] bond lengths compare well with that of $(Et_4N)_2$ [Pt(*i*-mnt)₂]²¹ but the S–C distances are slightly shorter than that expected for a typical S–C single bond



Fig. 3 (a) Dimeric structure and (b) crystal packing diagram of the complex cations of 3 showing alternating short and long Pt \cdots Pt distance of 3.753 Å (black dotted line) and 4.375 Å (red dotted line), respectively.



Fig. 4 (a) Perspective drawing of the complex cation of $[\{Pt(trpy)\}_2 \{\mu - (i-mnt)\}](PF_6)_2 \mathbf{4}$ with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 40% probability level. (b) Crystal packing showing the dimer-of-dimer structure of the complex cation of $\mathbf{4}$.

in a related complex, *cis*-(*E*)-[Pt(SPh)(PhSCSO)(PPh₃)₂] (Pt–S = 2.379 Å and S–C = 1.791 Å of the SPh moiety),²² indicating that there are some electron delocalization within the *i*-mnt moiety that is also commonly observed in other related platinum(II) diimine²⁰ and phosphine²³ complexes containing chelating mnt ligand. The C(1)–C(2) bond length of the *i*-mnt ligand is 1.37 Å, typical of a C=C double bond. The crystal packing of **4** reveals that the complex cations of **4** are arranged in a head-to-tail configuration with respect to each other [N(5)–Pt(2)–Pt(2)–N(5) torsion angle, 180°] and are extended along the *a* axis to form a one-dimensional infinite chain with alternating "short" and "long" intermolecular Pt…Pt contacts with Pt…Pt separations of 3.380 Å and 4.986 Å, respectively (Fig. 4(b)). The observation of short Pt…Pt

separation in a dimeric structure suggests the presence of some intermolecular $Pt \cdots Pt$ interactions between the neighbouring metal centres. Similar one-dimensional infinite chain comprising of dimer-of-dimer arrangement has also been reported in a related dinuclear complex, [{Pt(trpy)}_2(\mu-NHC(=O)Me)](OTf)_3.^{5g}

Electronic absorption spectroscopy

The electronic absorption spectra of complexes **1–8** show intense vibronic-structured bands at 274–348 nm with ε in the order of 10⁴ dm³ mol⁻¹ cm⁻¹ and broad absorptions at 382–570 nm in acetonitrile. Table 3 summarizes the electronic absorption spectral data. The high-energy structured bands at 274–348 nm are

Table 3 Photophysical data for the terpyridyl-crown precursors and dinuclear platinum(II) terpyridyl complexes

Complex	Medium (T/K)	$\lambda_{\rm abs}/{\rm nm}~(\varepsilon_{\rm max}/{\rm dm^3~mol^{-1}~cm^{-1}})$	$\lambda_{\rm em}/{\rm nm} \left(\tau_{\rm o}{}^{a}/{\rm \mu s}\right)$
1b	CH ₃ CN (298) Solid (77)	290 (41 410), 322 (19 380), 340 (18 250), 430 (22 790)	630 (0.2) 630 (0.4) 585 (58 4) 660 (4 2)
2b	CH ₃ CN (298) Solid (77)	290 (40 045), 322 (18 860), 340 (17 865), 430 (21 845)	640 (0.3) 650 (0.8) 575 (30.2) 670 (3.5)
3	CH ₃ CN (298) Solid (298) Solid (77) Chase ^b (77)	274 (53 150), 314 (24 150), 332 (22 500), 348 (23 650), 382 sh (4150), 570 (1810)	713 (39.2), 070 (3.3) Non-emissive 708 (<0.1) 707 (0.8) 470 (26.3) 675 (4.0)
4	CH ₃ CN (298) Solid (298) Solid (77) Glass ⁶ (77)	274 (38 370), 314 (23 200), 336 (29 320), 378 (18 300), 466 (4810)	Von-emissive 725 (<0.1) 740 (1.0) 470 (11 8) 640 (4 7)
5	$CH_3CN (298)$ Solid (77) Classb (77)	292 (69 540), 340 sh (41 590), 380 (30 810), 430 (36 540), 486 sh (21 520)	640 (<0.1) 745 (0.1) 545 (34.8) 670 (5.9)
6	$CH_3CN (298)$ Solid (77) Glass ⁶ (77)	290 (74 260), 340 sh (45 850), 378 (32 790), 432 (40 010), 488 sh (17 190)	640 (<0.1) 750 (0.2) 545 (35.3), 665 (7.8)
7	CH_3CN (298) Solid (77) Glass ^b (77)	290 (88 780), 340 (74 040), 414 (49 960), 470 (20 520)	635 (<0.1) 735 (0.2) 540 (42.1) 685 (4.2)
8	CH ₃ CN (298) Solid (77) Glass ^b (77)	292 (75 910), 340 (64 960), 416 (44 530), 470 (18 650)	645 (<0.1) 735 (0.2) 540 (39.9), 690 (5.3)

^a Luminescence lifetime values were measured with an uncertainty of ±10%. ^b In butyronitrile glass.

assigned as intraligand (IL) transitions of the terpyridine ligands and/or sulfur-containing ligands, since similar absorptions have also been observed in [Ir(trpy)₂]³⁺²⁴ and Zn(trpy)Cl₂,²⁵ and the free terpyridine and sulfur-containing ligands. In view of the electronic absorption study of [Pt(trpy)Cl]⁺ in acetonitrile, which shows that the lowest energy absorption band occurs at ca. 400 nm with an extinction coefficient of 10³ dm³mol⁻¹cm⁻¹, the low-energy absorption band at 430 nm of the mononuclear complexes 1 and 2 containing the terpyridine ligand substituted with ethynylbenzene is assigned as an admixture of $d\pi(Pt) \rightarrow \pi^*(trpy)$ metal-toligand charge transfer (MLCT) transition and IL transition of the terpyridyl ligand. It is worthwhile to note that the extinction coefficient of this band ($\varepsilon \ge 10^4 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) is much larger than what one would have expected for a pure MLCT transition, suggesting that this band contains some mixing of the more intense IL transition of the terpyridyl ligand. The occurrence of this IL transition at such low energy region is ascribed to the lower π^* orbital energy of the more conjugated terpyridyl ligand as a result of the attachment of the substituted ethynylbenzene. For complex 3 that contains the 1,3-benzenedithiolate bridge, the low-energy broad absorption band at 570 nm is tentatively assigned as a $p\pi(SC_6H_4S-1,3) \rightarrow \pi^*(trpy)$ ligand-to-ligand charge transfer (LLCT) transition. Similar assignments have also been made for the low-energy absorption band at ca. 520-572 nm in other related platinum(II) terpyridyl complexes containing aromatic thiolates.^{3h,5f} For the dinuclear complexes **4–8**, there is an additional lowest energy absorption band when compared to the electronic absorption spectra of the corresponding mononuclear chloro-counterparts. With reference to previous studies on dinuclear platinum terpyridyl systems,5 such low-energy absorption bands at 466-488 nm for complexes 4-8 are tentatively assigned as $d\sigma^*(Pt_2) \rightarrow \pi^*(trpy)$ metal-metal-to-ligand charge transfer (MMLCT) transition, probably with some mixing of a $p\pi(mnt)$ or $p\pi(dtc)$ to $\pi^*(trpy)$ LLCT character. Although the energy difference between the lowest energy absorption bands in 3 and 4 may be rationalized by the presence of two electron-withdrawing cyano groups on the *i*-mnt bridging ligand, which renders it less electron-rich than the 1,3-benzenedithiolate, as both the 1,3-benzenedithiolate and *i*-mnt bridging ligands of 3 and 4, respectively, are dianionic ligands, it is believed that an assignment of the low-energy absorption band of 4 as predominantly MMLCT in character mixed with some LLCT transition is more appropriate in light of the comparable absorption energy to other related dinuclear platinum(II) terpyridyl complexes.5 In addition, the presence of intramolecular Pt ··· Pt contact revealed in the solidstate structure of 4 is further supportive of the HOMO as being $d\sigma^*$ orbital in nature that results from the intramolecular interaction between the two platinum metal centres, while the lack of intramolecular Pt ··· Pt contact in 3 due to its anti-conformation eliminates the possibility of a MMLCT transition in solution state. The lower absorption energies for complexes 5 and 6 that contain substituted-terpyridine ligand than complex 4 are attributed to the electron-withdrawing abilities of the ethynylbenzo-15-crown-5 and 3,4-dimethoxyphenylethynyl moieties on the terpyridine ligand. The electronic absorption spectrum of 5 appears to be somewhat a superimposition of the spectra of the mononuclear complex 1 and the dinuclear complex 4 and Fig. 5 shows the electronic absorption spectra of 1, 4 and 5 in acetonitrile at 298 K. Complexes 7 and 8, similar to 5 and 6, are likely to show low-energy absorptions of



Fig. 5 Electronic absorption spectra of $[Pt(trpyC=C-benzo-15-crown-5)Cl]PF_6 1$ (-), $[{Pt(trpy)}_2{\mu-(i-mnt)}](PF_6)_2$ 4 (\cdots) and $[{Pt(trpyC=C-benzo-15-crown-5)}_2{\mu-(i-mnt)}](PF_6)_2$ 5 (---) in acetoni-trile at 298 K.

a MMLCT nature that mixes with a LLCT character in view of the presence of short intramolecular $Pt \cdots Pt$ contact in the related [{Pt(trpy)}₂(μ -dtc)](PF₆)₃.^{5f} The lower absorption energies of the low-energy absorptions in **5** and **6** than the corresponding **7** and **8** are in line with the larger electron-donating property of *i*-mnt than the dtc ligand,²⁶ which would give rise to a lower energy LLCT transition that mixes into the MMLCT transition. The relatively large extinction coefficients for the low-energy bands in complexes **5–8** are also suggestive of a mixing of an IL and LLCT character into the MMLCT band.

Emission properties

All the complexes 1-8 show luminescence properties in various media and temperatures with the exception of 3 and 4, which are non-emissive in acetonitrile at room temperature (Table 3). In contrast to the related unsubstituted terpyridine complex, [Pt(trpy)Cl]⁺, which is non-emissive in room-temperature fluid solution, the mononuclear complexes, 1 and 2, exhibit intense emission at 630–640 nm upon excitation at $\lambda > 400$ nm in acetonitrile at room temperature and such emission band is independent of concentration in the range of 1×10^{-6} to $1 \times$ 10⁻⁴ M. Similar to the related complexes, [Pt(4'-Ar-trpy)Cl]⁺ (4'-Ar-trpy = 4'-aryl-substituted terpyridine derivative), which have also been reported to show emission in fluid solution at room temperature,³ⁱ the recovery of the luminescence property has been similarly attributed to the mixing of π - π * (Ar-trpy) ³IL character into the ³MLCT excited state, *i.e.* the emission of 1 and 2 in acetonitrile is derived from excited states of an admixture of $d\pi(Pt) \rightarrow \pi^*(trpyC=C-benzo-15-crown-5)^{-3}MLCT$ and metalperturbed $\pi \rightarrow \pi^*$ (trpyC=C-benzo-15-crown-5) ³IL character. The lack of luminescence of complexes 3 and 4 in acetonitrile at room temperature is attributed to the absence of such a mixing of ³IL character into the excited state. Other related dinuclear complexes, $[{Pt(trpy)}_2(\mu-L)]^{3+}$ (L = pyrazole, ^{5c} azaindole, ^{5c} diphenylformamidine,^{5c} arginine^{5c} and dtc^{5f}), were also found to show no significant emission intensity at room-temperature in fluid solution for the same reasons. The presence of a low-lying LLCT state in 3 may also be responsible for its lack of emissive behaviour in solution. The dinuclear complexes 5-8 exhibit broad emission bands at 635–645 nm upon excitation at $\lambda > 400$ nm in acetonitrile at room temperature. Although the related dinuclear platinum(II) complexes, $[{Pt(trpy)}_2(\mu-NHC(=O)Me)]^{3+5g}$ and $[{Pt(trpy)}_2(\mu-NHC(=O)Me)]^{3+5g}$ guanidine)]3+,5b exhibit emission bands at 600 and 620 nm,

respectively, which are attributed to the ³MMLCT excited state, such an assignment is not preferred for the emission of 5-8 at room-temperature in fluid solution since complex 4, with the same bridging *i*-mnt ligand as 5 and 6, is found to be non-emissive. In view of the fact that the emission bands of 5-8 occur at nearly the same energy as that of 1 and 2, together with the close resemblance of the excitation spectra of the mononuclear and dinuclear complexes, the emission of 5-8 is suggested to be derived from an excited state of predominantly $d\pi(Pt) \rightarrow \pi^*(trpyC=C$ benzo-15-crown-5/trpyC≡CC₆H₃(OCH₃)₂-3,4) ³MLCT in nature, probably with some mixing of $\pi - \pi^*$ (trpyC=C-benzo-15-crown-5/trpyC=CC₆H₃(OCH₃)₂-3,4) ³IL character. The emission and excitation spectra of 1 and 5 in acetonitrile at room temperature are shown in Fig. 6. On the other hand, the emission bands of complex 3 with the dithiolate bridge in various media at room temperature or 77 K are assigned as derived from the excited state of triplet ³MLCT/³LLCT character.^{3h}



Fig. 6 Emission (a) and excitation (b) spectra of $[Pt(trpyC=C-benzo-15-crown-5)Cl]PF_6$ 1 (--) and $[{Pt(trpyC=C-benzo-15-crown-5)}_2(\mu-(i-mnt))](PF_6)_2$ 5 (---) in acetonitrile at 298 K.

Although complexes 1–8 all showed solid-state emission at 77 K, their emission origins are not the same, depending on the nuclearities and the nature of the bridging ligands. For the mononuclear complexes, 1 and 2, the emission bands at ca. 630-650 nm, which are vibronically structured with vibrational progressional spacings of ca. 1200 cm⁻¹ that are typical of the aromatic stretch in the ground state, are ascribed to phosphorescence derived from the metal-perturbed ³IL excited state. The solid-state emission of complexes 3 and 4 show a broad band at 708-725 nm at room temperature that shows a red shift in emission energies to 750-755 nm upon cooling to 77 K. This may be rationalized by the lattice contraction at low temperatures, leading to a shortening of the $Pt \cdots Pt$ intermolecular separations and hence, increased $Pt \cdots Pt$ interactions. Complexes 5-8 also show a low-energy emission at 760–785 nm in the solid-state at low temperature. Such low energy emissions in the solid-state for all the complexes are assigned as derived from triplet states of MMLCT character, resulting from the significant $Pt \cdots Pt$ interaction in the solid-state. Similar assignment has also been reported for other dinuclear platinum(II) terpyridyl complexes, such as $[{Pt(trpy)}_2(\mu-X)](PF_6)_3$ (X = pyrazole, azaindole, diphenylformamidine, canaverine, arginine)^{5c} in the solid states.

In 77 K butyronitrile glass of low concentrations (10⁻⁶ mol dm⁻³), complexes 3–8 all show highly structured emission bands at 470-545 nm with vibrational progressional spacings of ca. 1300 cm⁻¹, typical of the aromatic vibrational mode of the terpyridine ligand, and are tentatively assigned as derived from states of π^{π} - π^{*} (trpy) IL origin. Upon increasing the concentration, all the complexes show, in addition to the high-energy vibronicstructured emission, a broad emission band centred at 640-690 nm, with an obvious preferential enhancement in the emission intensity of this band upon increasing the concentration from 10⁻⁶ to 10⁻⁴ mol dm⁻³. As shown in Fig. 7 for 5, the excitation spectra monitored at 540 nm and 685 nm appeared different, indicating that the two emission bands are of different origins. Thus the broad emission bands at ca. 640 – 690 nm that have comparable energy to the low-energy emission in solution, are similarly assigned as derived from triplet states of MMLCT character.



Fig. 7 Emission spectra of [{Pt(trpyC≡C-benzo-15-crown-5)}₂(μ -dtc)]-(PF₆)₃ 7 at concentrations 1×10^{-6} (—), 1×10^{-5} (---), and 1×10^{-4} (···) mol dm⁻³ in butyronitrile glass at 77 K. Insets: excitation spectra of monitored at 540 nm (—) and 685 nm (---).

Electrochemical properties

The electrochemical properties of 3-8 have been studied by cyclic voltammetry, while those of 1 and 2 were not studied due to their limited solubility in acetonitrile. The cyclic voltammogram of complex 3 in acetonitrile (0.1 M "Bu₄NPF₆) shows two quasireversible reduction couples at ca. -0.90 V and -1.50 V vs. SCE, which are assigned as terpyridine-based ligand-centred reductions. On the other hand, complexes 4-8 show, in addition to two quasireversible reduction couples at ca. -1.45 V and -1.65 V, two less negative reversible reduction couples at ca. -0.45 V and -0.73 V vs. SCE for 5 and 6 and at ca. -0.35 and -0.63 V vs. SCE for 7 and 8. The electrochemical data of the dinuclear platinum(II) terpyridyl complexes are summarized in Table 4. With reference to previous studies on platinum(II) terpyridyl systems,4e,f,7a the reduction couples at ca. -1.45 V and -1.65 V are tentatively assigned as terpyridine-based reductions with some mixing of the Pt(II) metal character, while the other two reduction couples with less negative reduction potentials correspond to the metalperturbed *i*-mnt and dtc ligand-centred reductions as these two ligands are reported to undergo reduction at ca. -0.40, -0.65 V and -0.50,-0.80 V vs. SCE, respectively, in the literature.²⁶ The more

Table 4 Electrochemical data for dinuclear platinum(II) terpyridyl complexes in acetonitrile solution (0.1 M "Bu₄NPF₆) at 298 K^a

Complex	Oxidation $E_{\rm pa}$ /V vs. SCE ^b	Reduction $E_{1/2}$ /V vs. SCE ⁴
$\frac{1}{[{Pt(trpy)}_{2}(\mu-SC_{6}H_{4}S-1,3)](PF_{6})_{2}(3)}$	+1.02	-0.90
		-1.50
$[{Pt(trpy)}_{2}{\mu-(i-mnt)}](PF_{6})_{2}$ (4)	+1.50	-0.40
		-0.70
		-1.44
		-1.66
$[{Pt(trpyC=C-benzo-15-crown-5)}_{2}{\mu-(i-mnt)}](PF_{6})_{2}$ (5)	+1.46	-0.45
		-0.73
		-1.45
		-1.67
$[{Pt(trpyC=CC_6H_3(OCH_3)_2-3,4)}_2{\mu-(i-mnt)}](PF_6)_2 (6)$	+1.48	-0.44
		-0.73
		-1.45
		-1.66
$[{Pt(trpyC=C-benzo-15-crown-5)}_2(\mu-dtc)](PF_6)_3 (7)$	+1.50	-0.35
		-0.65
		-1.48
		-1.64
$[{Pt(trpyC=CC_6H_3(OCH_3)_2-3,4)}_2(\mu-dtc)](PF_6)_3$ (8)	+1.52	-0.35
		-0.63
		-1.44
		-1.65

^{*a*} Working electrode, glassy carbon; scan rate 100 mV s⁻¹. ^{*b*} E_{pa} refers to the anodic peak potential for the irreversible oxidation waves. ^{*c*} $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively.

negative reduction potentials for the terpyridine-based reductions in complexes **4–8** than complex **3** are in line with the more difficult reduction of the terpyridine ligand after the initial reductions of the dtc and *i*-mnt ligands. An irreversible oxidation wave at *ca.* +1.02 to +1.52 V is observed in all the dinuclear complexes studied, tentatively assigned as a Pt(II) to Pt(III) oxidation. It is interesting to note that complexes **5** and **6** are oxidized at a slightly less positive potential than the corresponding complexes **7** and **8**, in line with the poorer π -accepting ability and better electronrichness of *i*-mnt than dtc, as reflected by the more negative *i*-mnt ligand-centred reduction potentials than that of dtc. The poorer π -accepting property and more electron-rich nature of the *i*-mnt ligand would less stabilize the lower oxidation state, *i.e.* Pt(II), leading to a less positive potential for Pt(II) \rightarrow Pt(III) oxidation.

Cation-binding studies

The cation-binding behaviour of 5 and 7 have also been investigated by UV-vis absorption spectrophotometry. Upon addition of alkali metal cations to an acetonitrile solution of dinuclear platinum(II) terpyridyl-crown complexes 5 and 7, a UV-vis absorption spectral change was observed. Fig. 8 and 9 show the UV-vis absorption spectral traces upon addition of potassium hexafluorophosphate to a solution of 5 and 7, respectively, in which well-defined isosbestic points were observed. Spectrochemical recognition of guest metal ions is confirmed by the absence of spectral changes in the electronic absorption spectra of the control complexes 6 and 8. For the binding of KPF_6 , log K_s values of 3.45 (±0.01) and 3.10 (±0.01) were obtained for complexes 5 and 7, respectively, according to eqn (1). The 1 : 1 stoichiometry for K⁺ ion-binding is evidenced by the close agreement of the experimental data with the theoretical fit (Fig. 8 and 9 inserts for 5 and 7, respectively), and has further been confirmed by the method of continuous variation, where a break point at a mole fraction of



Fig. 8 Electronic absorption spectral traces of [{Pt(trpyC=C-benzo-15-crown-5)}₂{ μ -(*i*-mnt)}](PF₆)₂ **5** (2.5 × 10⁻⁵ mol dm⁻³) in acetonitrile (0.1 mol dm⁻³ "Bu₄NPF₆) upon addition of KPF₆ (path length = 1 cm). The insert shows a plot of absorbance *vs.* [K⁺] monitored at λ = 480 nm (\blacksquare) and its theoretical fit (\frown).

0.5 is observed. Since the ionic diameter of the K^+ ion is too large to fit into the cavity of the benzo-15-crown-5, the 1 : 1 complexation ratio may suggest that the K^+ ion is sandwiched between the two benzo-15-crown-5 units within the dinuclear platinum complex. Similar binding model has also been observed in dinuclear gold(1) complexes.⁹ The binding constant for K^+ ion-binding of complex 7 is found to be smaller than that of complex 5. This may be rationalized by the lower positive charge borne on complex 5, which would give rise to a stronger ion-binding affinity for metal ions and hence a larger binding constant. In case of Na⁺ ionbinding studies, the lack of well-defined isosbestic points in the UV-vis spectral traces and the absence of a satisfactory fit to eqn (1) suggest that the binding of Na⁺ is not in a 1 : 1 stoichiometry,

Complex	Ion cluster, m/z
5	911 {[{Pt(trpyC=C-benzo-15-crown-5)} ₂ (μ -(<i>i</i> -mnt))·2Na](ClO ₄) ₂ } ²⁺ 1907 {{Pt(trpyC=C-benzo-15-crown-5)} ₂ (μ -(<i>i</i> -mnt))·Kl(PF ₄) ₃ +
7	2013 {{ $Pt(trpyC=C-benzo-15-crown-5)}_{2}(\mu-(i-mnt))$ ·Ba](ClO ₄) ₃ }* 990 { $Pt(trpyC=C-benzo-15-crown-5)$ ($\mu-dtc)$ ·Na]ClO ₄ }*
	1051 {[Pt(trpyC≡C-benzo-15-crown-5)(µ-dtc)·K]PF ₆ } ⁺ 1203 {[Pt(trpyC≡C-benzo-15-crown-5)(µ-dtc)·Ba](ClO ₄) ₂ } ⁺



Fig. 9 Electronic absorption spectral traces of [{Pt(trpyC=C-benzo-15-crown-5)}₂(μ -dtc)](PF₆)₃ 7 (2.5 × 10⁻⁵ mol dm⁻³) in acetonitrile (0.1 mol dm⁻³ "Bu₄NPF₆) upon addition of KPF₆ (path length = 1 cm). The insert shows a plot of absorbance *vs.* [K⁺] monitored at $\lambda = 476$ nm (\blacksquare) and its theoretical fit (\frown).

but probably a mixture of 1 : 1 and 1 : 2 complex-to-sodium ion binding. It is interesting to note that the binding model of the dinuclear platinum(II) complexes is found to be completely different from that of the mononuclear species, $[Pt(trpy)(S-benzo-15-crown-5)]PF_6^{6a}$ and $[Pt(trpy)(C=C-benzo-15-crown-5)]PF_6^{7a,j}$ in which a 1 : 1 complexation stoichiometry is generally observed with Na⁺ ions instead of K⁺ ions.

The ion-binding studies have further been confirmed by positive ESI-mass spectrometry. Table 5 summarizes the ion cluster peaks for the ion-bound adducts of the dinuclear platinum(II) terpyridyl crown ether-containing complexes, 5 and 7, and alkali metal cations. A 1:1 adduct was observed for the binding of 5 with K^+ and Ba^{2+} , while for Na⁺, only 1 : 2 adducts were observed. However, for the binding studies of 7, only a fragment of the monomeric species {Pt(trpyC=C-benzo-15-crown-5)(μ -dtc)}⁺ was observed with the formation of 1 : 1 adducts of NaClO₄, KPF₆ and $Ba(ClO_4)_2$. This can be attributed to the weakly bound nature of the carbamate ligand to the platinum(II) centre, which can easily undergo fragmention by ionization. Similar to the electronic absorption binding studies, crown-free analogues 6 and 8 did not show the presence of such ion-bound species upon the addition of metal ions, providing further supporting evidence for the binding of cations to the crown moieties.

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