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Dinuclear platinum(II) 4,6-diphenyl-2,2′-bipyridine complexes tethered by a rigid bridging ligand: synthesis and photophysics in solution and in LB film†

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Two dinuclear platinum(II) 4,6-diphenyl-2,2′-bipyridine (CˆNˆN) complexes (**1** and **2**) with a rigid bridging ligand *cis*-1,2-bis(diphenylphosphino)ethylene were synthesized and their photophysical properties were systematically investigated in solution for **1** and **2** and in LB film for **2**. Similar to their corresponding mononuclear complexes, both complexes exhibit intense $^1\pi,\pi^*$ absorption in the UV region and a broad, moderate absorption band in the visible region, which likely stems from the mixed ^{1}MLCT (metal-to-ligand charge transfer), ^{1}ILCT (intraligand charge transfer) and $^1\pi,\pi^*$ transitions. Both complexes are emissive in solutions at room temperature and in glassy matrix at 77 K. The emitting state is tentatively assigned as ^{3}MLCT for **1** and ^{3}MLCT/^{3}ILCT/$^3\pi,\pi^*$ for **2** at room temperature. At 77 K, the emission observed for **1** is mainly from the emissive ground-state aggregates, which is concentration dependent; while in **2** the emission from the monomer dominates. Unlike the dinuclear platinum complex with flexible bridging ligand diphenylphosphinoethane, the electronic absorption and emission energies of **1** and **2** at room temperature are independent of their concentration, indicating a fixed conformation for these two complexes. In addition, the presence of alkoxyl substituents on the diphenylbipyridine ligands causes a bathochromic shift of the lowest-energy absorption band and the emission band at room temperature for **2**, presumably due to the involvement of the ILCT character into the lowest excited states. The presence of alkoxyl substituents in **2** also makes **2** amphiphilic, allowing for the fabrication of LB films of **2**. The electronic absorption and emission characteristics in the LB films of **2** are quite similar to those in solutions, indicating no intermolecular Pt–Pt interactions occur in the LB films. The dinuclear complex without alkoxyl substituent (**1**) exhibits vapochromic behavior to heteroatom-containing volatile organic compounds (VOC's).

Introduction

Square-planar Pt(II) complexes have been studied extensively in recent years due to their unique spectroscopic properties.[1–25] In addition, their square-planar configuration can result in inter/intramolecular interactions that lead to self-quenching or cross-quenching through formation of excimer or exciplex,[26–29] ground-state aggregation, concentration-dependent emissive excited-state formation and a variety of photochemical reactivities.[24,30–32] These properties make d^8 Pt(II) complexes potential candidates as chemical sensors,[33–35] luminescent probes for biological macromolecules,[36] opto-electronic devices like organic light-emitting devices (OLEDs),[2–3,37–38] and chemical catalysts.[39–40] 6-Phenyl-2,2′-bipyridine (phbpy, CˆNˆN) ligand is a stronger σ-donor than 2,2′:6′,2″-terpyridine (NˆNˆN) and a better π-acceptor than 2,6-diphenylpyridine (CˆNˆC) ligands.[41] Stronger emission from platinum(II) phbpy complexes were generally observed compared to their corresponding platinum(II) terpyridine complexes. The emission properties of the platinum(II) phbpy complexes could be tuned by introducing different substituents on the phenylbipyridine ligand, or using different monodentate co-ligands. It can also be altered through inter-/intra-molecular interactions, in particular, the Pt–Pt or π–π interactions. For example, intermolecular interactions that influence the energy of the emitting state was observed in mononuclear Pt(II) complexes in solution due to oligomerization and excimer formation.[25] Such interactions give rise to new excited state(s), *i.e.* metal-metal-to-ligand charge transfer state (MMLCT).[42] Intramolecular Pt–Pt or π–π interactions have also been studied in a series of binuclear or trinuclear platinum(II) phbpy complexes tethered by polyphosphine bridging ligand by Che *et al.* and our group.[41–45] It is found that by varying the length of the bridging ligand, the extent of Pt–Pt and π–π interactions can be controlled. The complex tethered by bis(diphenylphosphino)methane (dppm) ligand exhibits the strongest Pt–Pt interactions, and consequently the MMLCT state becomes the lowest excited state.[45] This results in a deeper color for the complex and lowers the emission energy. Furthermore, our previous studies reveal that the non-linear transmission properties of the aforementioned binuclear complexes are affected by the degree of Pt–Pt and π–π interactions as well.[45] An additional interesting discovery from our previous studies was that the electronic absorption and emission characteristics of the dinuclear complexes with dppm and bis(diphenylphosphino)ethane (dppe) bridging ligand and the trinuclear complex with bis(diphenylphosphinomethyl)phenylphosphine (dpmp) bridging ligand were influenced by the concentration of solutions.[42,45]

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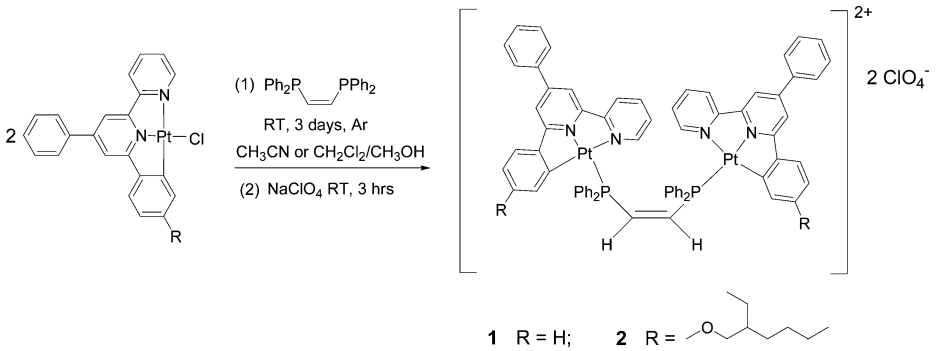
† Electronic supplementary information (ESI) available: The concentration-dependent electronic absorption spectra of **1** and **2** in CH_3CN; the emission spectra of **1** and **2** in different solvents at room temperature, and the time-resolved emission spectra of **1** and **2** at different concentrations in CH_3CN glassy solutions at 77 K. See DOI: 10.1039/c0dt00597e



Scheme 1 Synthetic scheme for Pt(II) dinuclear complexes **1** and **2**.

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With an increased concentration, the intramolecular Pt–Pt and π–π interactions increased, giving rise to stronger MMLCT absorption and emission bands. This phenomenon was tentatively attributed to the conformational change of the complex from a "twisted" conformation at lower concentrations to a "face-to-face" confirmation at higher concentrations. Such a concentration-dependent photophysical behavior may cause complication for future practical applications. To confirm this "conformational transformation" speculation and to avoid complication in future application, we designed and synthesized a new dinuclear complex $[Pt_2(dphbpy)_2(\mu\text{-dppethylene})](ClO_4)_2$ (**1**) (the structure and the synthetic route are shown in Scheme 1) with a rigid bridging ligand, bis(diphenylphosphino)ethylene that has the similar length as dppe but a fixed conformation. Its photophysical properties, especially the UV-vis and emission characteristics at different concentrations were systematically investigated.

In addition, our previous work on mononuclear platinum C^N^N complexes discovered that introducing an alkoxyl substituent on the 6-phenyl ring could significantly increase the emission quantum yield and lifetime, and make the complex amphiphilic to form LB films.[46,47] To verify if this strategy also applies to the dinuclear complex, a dinuclear platinum(II) dphbpy complex (**2**) with alkoxyl substituents on the 6-phenyl rings has been synthesized and investigated as well. It is expected that complex **2** could show stronger emission at room temperature and 77 K than complex **1**, and could form emissive LB films.

Experimental

Synthesis

The synthesis of the respective monomers, platinum(II) dphbpy chloride complexes, follows the procedures described in the literature[5] and by our group.[46,47] The synthetic route for **1** and **2** is provided in Scheme 1. All solvents (analytical grade) were purchased from VWR and used without further purification unless otherwise stated. All the chemicals for the synthesis of monomers and *cis*-1,2-bis(diphenylphosphino)ethylene were purchased from Alfa Aesar and used as supplied. The synthesized compounds were characterized by ^{1}H NMR (Varian, 400 MHz) and high-resolution mass spectrometry (Bruker BioTOF III). Elemental analyses were carried out by NuMega Resonance Laboratories, Inc. in San Diego, California.

1. The corresponding monomer dphbpyPtCl (0.062 g, 0.12 mmol) and *cis*-1,2-bis(diphenylphosphino)ethylene (0.023 g, 0.06 mmol) were dissolved in 20 mL methanol–acetonitrile solution (v/v = 1 : 1) at room temperature, and the mixture was stirred at room temperature under argon atmosphere for 72 h. The reaction was monitored by UV-vis spectroscopy periodically. After the reaction was ceased, 5 mL saturated methanolic solution of $NaClO_4$ was added to the clear reaction mixture and stirred at room temperature for 3 h. Then the reaction mixture was reduced to 5 mL. The yellow precipitates were filtered and washed with water and diethyl ether. The crude product was further purified by recrystallization from dichloromethane and diethyl ether to afford 0.035 g yellow amorphous solid (yield: 38%). ^{1}H NMR (CD_3CN, 400 MHz): δ 8.44 (d, J = 5.2 Hz, 4H), 8.11 (td, J = 4.4 Hz, 7.6 Hz, 4H), 8.01 (d, J = 8.0 Hz, 4H), 7.78–7.75 (m, 8H), 7.71 (s, 4H), 7.65–7.59 (m, 16H), 7.38 (m, 2H), 7.22 (d, J = 7.2 Hz, 2H), 6.99 (m, 6H), 6.83 (d, J = 6.0 Hz, 2H) ppm. Anal. Calcd for $C_{70}H_{52}Cl_2N_4O_8P_2Pt_2$: C, 52.54; H, 3.28; N, 3.50. Found: C, 52.13; H, 2.95; N; 3.88.

2. A solution of 0.070 g (0.11 mmol) platinum dphbpy chloride monomer with the alkoxyl substituent and 0.021 g (0.05 mmol) *cis*-1,2-bis(diphenylphosphino)ethylene in 20 mL dichloromethane–methanol (v/v = 1 : 1) was stirred at room temperature under argon atmosphere for 72 h. The reaction was monitored by UV-vis spectroscopy. After completion of the reaction, metathesis reaction was carried out by addition of 5 mL saturated methanolic solution of $NaClO_4$ in order to change the counterion to ClO_4^-. The crude product was collected by filtration, washed with water and diethyl ether and further purified by recrystallization from dichloromethane and diethyl ether to afford 0.032 g yellow-orange amorphous solid. (yield: 32%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (m, 1H), 8.01 (m, 3H), 7.89 (d, 2H), 7.56–7.35 (m, 31H), 7.09 (d, 3H), 6.62 (m, 2H), 6.39 (d, 2H), 6.29 (m, 2H), 5.66 (s, 2H), 3.63 (m, 2H), 3.45 (m, 2H), 1.31–1.22 (m, 18H), 0.94–0.83 (m, 12H). ESI-MS m/z calcd for $[C_{86}H_{84}Cl_2N_4O_{10}P_2{}^{195}Pt_2]^{2+}$: 828.7687, Found: 828.7671 (100%). Anal. Calcd for $C_{86}H_{84}Cl_2N_4O_{10}P_2Pt_2\cdot 0.7CH_2Cl_2$: C, 54.29; H, 4.45; N, 2.92. Found: C, 53.82; H, 4.46; N; 3.39.

Photophysical measurements

For photophysical studies in solution, HPLC grade acetonitrile was used. UV-vis spectra were obtained using a Shimadzu 2501 PC UV-vis spectrophotometer. Steady state emission and excitation spectra at room temperature were measured using a SPEX

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Fluorolog-3 fluorometer/phosphorometer. The solutions were degassed with argon for 30 min before each measurement. The time-resolved emission spectra at 77 K, the emission lifetime and the triplet transient difference absorption spectra were measured on an Edinburgh LP920 laser flash photolysis spectrometer. The third harmonic output (355 nm) of a Nd:YAG laser (Quantel Brilliant, pulsewidth (fwhm) = 4.1 ns, repetition rate = 1 Hz) was used as the excitation source. For the time-resolved emission measurement at 77 K, an ICCD camera (Andor Technology, *i*Star 734) was used as the detector.

Partial saturation method was used to measure the triplet excited-state molar extinction coefficient and triplet quantum yield.[48,49] Excitation energy at 355 nm was increased gradually while monitoring the optical density at 550 nm. Eqn (1) was used to fit the experimental data to obtain the ε_T and Φ_T.[48,49]

$$\Delta OD = a(1 - \exp(-bI_p)) \quad (1)$$

where ΔOD is the optical density change at 550 nm, I_p is the pump intensity in Einstein cm^{-2}, $a = (\varepsilon_T - \varepsilon_0)dl$, and $b = 2303\varepsilon_0^{ex}\Phi_T/A$. ε_T and ε_0 are the absorption coefficients of the excited state and the ground-state at 550 nm respectively, ε_0^{ex} is the ground-state absorption coefficient at the excitation wavelength of 355 nm, d is the concentration of the sample (mol L^{-1}), l is the thickness of the sample excited by the excitation beam (namely the diameter of the excitation beam), and A is the area of the sample irradiated by the excitation beam.

LB film preparation and characterization

Glass slides were used as the substrate to deposit LB films. Hydrophilic treatment of glass was carried out by cleaning it using detergent with repeated sonication followed by washing with water. The slides were then soaked in concentrated H_2SO_4 for about one hour. Finally, the slides were washed with large amount of ultra pure water. KSV minitrough (Teflon coating, 7.5 × 30 × 1 cm^3) was used to measure the isotherm and prepare the LB film. Ultra pure water (18.2 MΩ·cm^{-1}) was used to carry out all the LB film experiments. Platinum complex solution (0.19 mM in CH_2Cl_2) was spread over the pure water subphase at a constant temperature of 25 ± 1 °C. The subphase was left undisturbed for 25 min for the solvent to evaporate. The isotherm was plotted at a compression rate of 5 mm min^{-1}. The film was transferred from the subphase to the hydrophilic substrate by the dipping method. The deposition was carried out and the transfer ratio observed was near unity.

AFM images of the LB films prepared were obtained on a Veeco DI-3100 with a silicon nitride probe by tapping mode in order to study the surface morphology of the LB films.

Results and discussion

UV-vis absorption

The UV-vis absorption spectra of **1** and **2** are shown in Fig. 1. The spectra consist of high intensity absorption bands below 400 nm, which can be attributed to ligand $^1\pi,\pi^*$ transitions,[23,45] and a broad, moderately intense absorption band in the visible region. With reference to the TDDFT calculations performed on the corresponding mononuclear platinum C^N^N complexes reported by our group previously,[46] we tentatively assign these low-energy

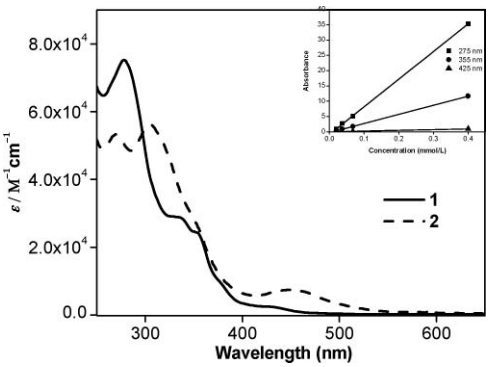

Fig. 1 Electronic absorption spectra of **1** and **2** in acetonitrile (inset: absorbance *vs.* concentration for **1** at different wavelengths).

absorption bands in **1** and **2** to mixed ^{1}MLCT/^{1}ILCT/$^1\pi,\pi^*$ transitions (^{1}ILCT refers to intraligand charge transfer from the phenylpyridine component to the bipyridine component within the C^N^N ligand). However, ^{1}ILCT transition would dominate the lowest singlet excited state of **2** due to the electron-donating alkoxyl substituent in **2**. This could be supported by its notably broadened and more intense low-energy absorption band in comparison to that of **1**, which is consistent with that observed in the mononuclear platinum dphbpy chloride complex with the alkoxyl substituent that increases the ^{1}ILCT contribution.[46] In line with the dinuclear platinum complexes tethered by dppe ligand, the molar extinction coefficients of **1** and **2** are much higher than that of their mononuclear congener with the triphenylphosphine ligand.[24,50] However, unlike the dinuclear complex tethered by the dppe ligand, **1** and **2** does not exhibit concentration-dependent UV-vis spectra. The absorption of **1** and **2** obeys Lambert–Beer's law in the concentration range studied (10^{-4}–10^{-6} mol L^{-1}) (see inset in Fig. 1 and ESI Fig. S1†). Therefore, the formation of intermolecular dimer or oligomers can be excluded, and the conformation can be considered as "locked" with the rigid bridging ligand so that no conformational transformation occurs with varied concentration.

Fig. 2 shows the UV-vis absorption spectra of **1** and **2** in different solvents (Fig. 2). Unlike many other platinum(II) polypyridine complexes reported in the literature,[2,18–25,51–59] **1** and **2** do not exhibit a drastic solvatochromic effect. Especially for **2** almost no change was observed in the three solvents tested (no other less-polar solvents could be used due to its limited solubility in those solvents). This feature is consistent with that observed from its corresponding mononuclear platinum chloride complexes due to the delocalization of the electron-density in the excited state or alternatively, due to the admixture of configurationally distinct transitions (^{1}MLCT, ^{1}ILCT, $^1\pi,\pi^*$, *etc.*) into the lowest excited state.[46] However, a blue-shift of the low-energy absorption band in **1** is apparent in more polar methanol solution than in the other solutions, which is typical for platinum complexes with a metal-to-ligand charge transfer character in their lowest excited state.[2,18–25,51–59] This implies that the electron-density in the excited-state of **1** does not delocalize as much as that in **2**; or alternatively, the contribution from ^{1}MLCT transition is more in **1** than in **2**, which is consistent with the TDDFT calculation result reported for the corresponding mononuclear platinum complexes with and without alkoxyl substituent.[46]

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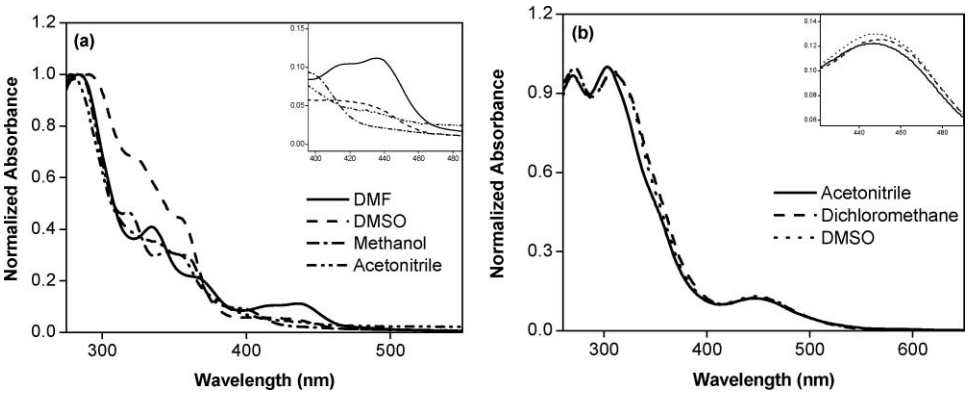

Fig. 2 Electronic absorption of (a) **1** and (b) **2** in different solvents.

Emission

Complexes **1** and **2** are emissive both at room temperature and at 77 K. Upon excitation at 425 nm for **1** and 445 nm for **2** in CH_3CN solution at room temperature, a broad structureless emission band was observed at 567 nm and 607 nm for **1** and **2**, respectively (Fig. 3). The lifetime of this band is approximately 80 ns for **1**, and 2.7 μs for **2** in CH_3CN solution with $A_{abs} \approx 0.07$ in a 1 cm cuvette at 436 nm (listed in Table 1). For **1**, both its emission energy and lifetime are in line with those of its corresponding mononuclear complexes with PPh_3 and Cl co-ligand.[23,24,46] Therefore, the emission band at ~570 nm could be tentatively attributed to the ^{3}MLCT state. For **2**, the emission energy of 607 nm is similar to that of its corresponding mononuclear platinum chloride complex[46] but its emission lifetime is much longer than that of the mononuclear complex. The latter phenomenon is probably associated with the "face-to-face" nature of the two (C^N^N)Pt components, which could prevent the approach of solvent molecules from one side and thus reduces the solvent quenching effect. This notion could be supported by the much longer lifetime of **1** and **2** (~3.0 μs for **1** and ~3.6 μs for **2**, see ESI Table S1†) in CH_2Cl_2 in comparison to their respective mononuclear complex with Cl or PPh_3 co-ligand.[23,24,46] However, the solvent quenching effect in solvents with increasing donor strength, such as CH_3CN, DMF and DMSO, is quite different for **1** and **2**. As shown in ESI Fig. S2 and Table S1,† the solvent quenching effect in CH_3CN, DMF and DMSO is greatly reduced in **2** than in **1**, which implies the different nature of the emitting state for these two complexes. The similar emission energy of **2** to that of its corresponding mononuclear complex suggests that their emitting states are similar, *i.e.* the emitting state for **2** admixes ^{3}MLCT, ^{3}ILCT and $^3\pi,\pi^*$ characters, possibly with the ^{3}ILCT and $^3\pi,\pi^*$ characters predominates. This is distinct from that of **1**, where ^{3}MLCT is the predominant contributor. The increased ^{3}ILCT and $^3\pi,\pi^*$ characters in the emitting state of **2** lead to the reduced solvent quenching effect, the minor solvent effect on the emission energy, and the longer lifetime in CH_3CN for **2**.

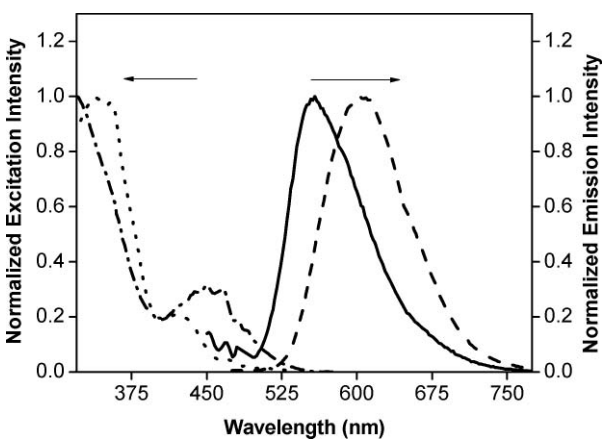

Fig. 3 Normalized emission (solid line (—) for **1** and dashed line (---) for **2**) and excitation spectra (dotted line (···) for **1** and dash dotted line (-·-) for **2**) of **1** and **2** in acetonitrile solution at R.T. The excitation wavelength for emission spectral measurement was 425 nm for **1** and 450 nm for **2**, and the excitation spectra were monitored at the emission wavelength of 555 nm for **1** and 600 nm for **2**. The complex concentration used was approximately 1×10^{-5} mol L^{-1}.

Comparing the emission energy and lifetime of **1** and **2**, it is clear that the alkoxyl substituents in the dinuclear complex induce the red-shift of the emission band and reduced solvent quenching effect due to the increased involvement of the ^{3}ILCT/$^3\pi,\pi^*$ characters into the emitting state, which is in line with that observed in the respective mononuclear complexes.[46] This trend is also consistent with the trend observed in the UV-vis absorption spectra.

Because one of the ultimate goals of this work is to verify whether a rigid bridging ligand could prevent conformational change at varied concentrations, the concentration-dependent emission was investigated for **1** and **2** in acetonitrile. As shown in Fig. 4 and the ESI Fig. S3,† the emission energies of **1** and **2** are independent of the concentrations of solutions, which is obviously different from that observed for the corresponding dinuclear platinum complex tethered by di(phenylphosphino)ethane (dppe).[45] This implies that the conformations of complexes **1** and **2** with rigid bridging ligand are "locked". In addition, the emission intensity increases with increased concentration from 3.7×10^{-5} mol L^{-1} to 4.0×10^{-4} mol L^{-1} for **1** and from 1×10^{-6} mol L^{-1} to 1×10^{-4} mol L^{-1} for **2**, and the lifetimes remain the same for these solutions. These facts indicate that no self-quenching occurs in the concentration range studied for **1** and **2**.

1 and **2** are also emissive at 77 K in acetonitrile glassy solutions. As shown in Fig. 5, the emission energy of **1** at 77 K is concentration-dependent. At a lower concentration of 3.7 $\times 10^{-5}$ mol L^{-1}, two emission bands appear at 500 nm (τ = 9.4

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Table 1 Photophysical parameters for **1** and **2** in CH_3CN

Complex	λ_{abs}/nm (ε/M^{-1} cm^{-1})[a]	λ_{em}/nm (τ_{em}/ns; Φ_{em}) R.T.[b]	λ_{em}/nm (τ_{em}/μs) 77 K	λ_{T1-Tn}/nm (ε_{T1-Tn}/M^{-1}cm^{-1}; τ_T/ns)[d], Φ_T	λ_{em}/nm (τ_{em}/μs) LB films[e]
1	278 (75050), 335 (28700), 355 (23880), 425 (2550)	567 (80; 0.01)	500 (9.4)[c], 660 (2.4)	385, 550 (17770; 76), 0.08	—
2	270 (52880), 305 (56290), 450 (7390)	607 (2670; 0.25)	600 (5.8)[a]	385, 550 (3370; 1700), 0.12	600 (2.5)

[a] Measured at a concentration of 1×10^{-5} mol L^{-1}. [b] Measured in a solution with $A \approx 0.07$ at 436 nm in a 1 cm cuvette. [c] Measured at a concentration of 3.7×10^{-5} mol L^{-1}. [d] Measured at a concentration of 5×10^{-5} mol L^{-1} for **2**. [e] Measured for 11 layer LB film.

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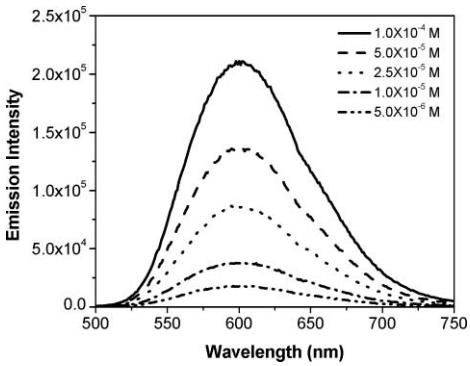

Fig. 4 Concentration-dependent emission spectra of **2** at R.T. in CH_3CN. λ_{ex} = 445 nm.

μs) and 660 nm (τ = 2.4 μs), with the low-energy emission band dominates. When the concentration is increased to 6.8×10^{-5} mol L^{-1}, the relative intensity of the 500 nm band decreases and the low-energy band red-shifts to 700 nm (τ = 2.8 μs). At a higher concentration of 4.0×10^{-4} mol L^{-1}, the high-energy band at 500 nm disappears, accompanied by a new emission band appearing at 740 nm with a lifetime of 0.93 μs. Due to the drastically different lifetimes for these two bands, the origin of these two bands is obviously different. The high-energy band could be tentatively regarded as a ^{3}MLCT emission in view of the similar emission energy and lifetime to other mononuclear platinum complexes with a ^{3}MLCT emitting state at 77 K.[5,8,14,16,19,22,24] In contrast, the low-energy band likely emanates from an emissive ground-state aggregates, which is concentration-dependent. The higher the concentration, the higher the degree of aggregation and the further red-shift of the emission band. The appearance of the ground-state aggregation at 77 K but not at room temperature suggests that the association constant for the aggregation process could be too small to be observed at room temperature.

For complex **2**, the emission spectrum at 77 K (Fig. 5) is somewhat narrower comparing to that at room temperature. The emission lifetime is approximately 6.0 μs. Considering the similar emission energy at room temperature and at 77 K, the emitting state at 77 K for **2** could be tentatively assigned as the same emitting state at room temperature, *i.e.* ^{3}MLCT/^{3}ILCT/$^3\pi,\pi^*$.[46,47] However, unlike what was observed at room temperature, the emission of **2** at 77 K exhibits concentration-dependent. With increased concentration, a low-energy tail appears at 750 nm for the solution of 5.0×10^{-5} mol L^{-1}, and this tail is further red-shifted to approximately 800 nm at a concentration of 1.0×10^{-4} mol L^{-1}. The lifetimes of these low-energy tails are approximately 4.0 μs. Similar to that discussed in the previous paragraph for complex **1**, the low-energy tail is also tentatively assigned to emissive ground-state aggregates. Comparing the relative intensity of the lower-energy band to that of the higher-energy band for **1** and **2**, it is clear that **1** is much easier to aggregate than **2** does at 77 K. This difference should be attributed to the presence of the branched alkyl chains in **2** but not in **1**, which would reduce the intermolecular π–π interactions and thus decrease the tendency of aggregation in **2**.

Triplet transient difference absorption

Our emission studies discussed in the previous section indicate that complex **2** has long-lived triplet excited state. For complex **1**, even though the lifetime of its triplet emitting excited state is not as long as one expects for a triplet excited state, it is still much longer than

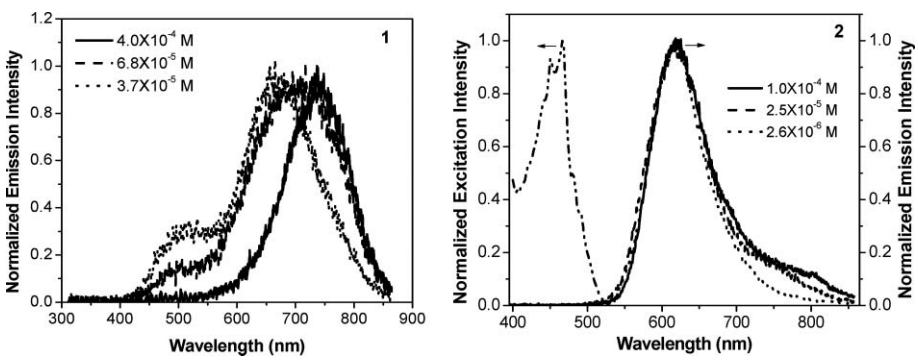

Fig. 5 Concentration-dependent emission spectra of **1** and **2** in acetonitrile glassy solutions at 77 K. The spectra were recorded using an ICCD camera on a LP920 laser flash photolysis spectrometer at zero time delay. λ_{ex} = 355 nm. The excitation spectrum for **2** was recorded on a Spex Fluorolog-3 Phosphorometer at the emission maximum ($c = 1 \times 10^{-5}$ mol L^{-1}).

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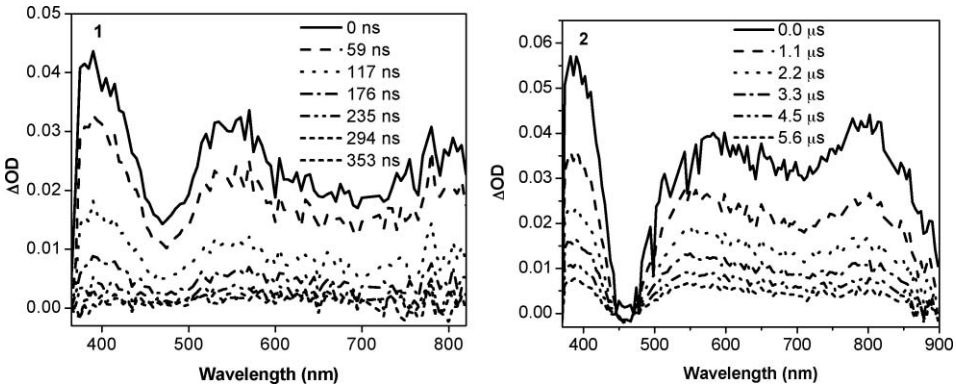

Fig. 6 Time-resolved triplet transient difference absorption spectrum of **1** (3.7×10^{-5} mol L^{-1}) and **2** (5×10^{-5} mol L^{-1}) in acetonitrile at R.T. λ_{ex} = 355 nm. The time indicated in the legend is the time delay after the excitation.

the excitation pulse width (4.1 ns). Therefore, triplet excited-state absorption is possible for ns excitation. To demonstrate this, time-resolved triplet transient difference absorption spectra of **1** and **2** were measured on the LP920 laser flash photolysis spectrometer and the results are shown in Fig. 6.

For both complexes the spectra consist of a relatively narrow absorption band at *ca.* 385 nm, and two broad, positive absorption bands at *ca.* 550 nm and 800 nm. A very weak bleaching band around 450 nm is observed for **2**. With reference to the transient absorption spectra of the mononuclear platinum terpyridyl complexes reported by Castellano *et al.* the band at 385 nm could mainly arise from the coordinated CˆNˆN anion in the ^{3}MLCT state, while the broad bands at 550 nm and 800 nm originates from the ^{3}MLCT state.[18] This assignment is in accordance with the reduced lifetime measured through the decay of the transient absorption compared to that obtained through the decay of the emission, which indicates the charge-transfer character of the excited state that gives rise to the transient absorption. The triplet excited-state absorption coefficient and the triplet quantum yield were measured by the partial-saturation method. Through fitting of the experimental data by eqn (1) (Fig. 7), the triplet excited-state absorption coefficient of **2** is obtained to be 3370 M^{-1} cm^{-1} at 550 nm, and the quantum yield (Φ_T) of the triplet excited state giving rise to the transient absorption is measured to be 0.12. For complex **1**, the ε_{T1-Tn} is 17770 M^{-1} cm^{-1} at 550 nm, and the Φ_T is 0.08.

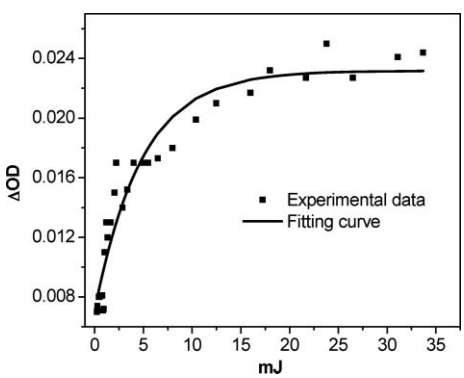

Fig. 7 Experimental data and fitting curve of the variation of the transient absorbance at 550 nm for **2** as a function of laser pulse energy after excitation at 355 nm. Complex concentration is ~1.6×10^{-5} mol L^{-1} in acetonitrile.

Preparation, characterization and photophysical studies of LB films of 2

We have demonstrated that mononuclear CˆNˆN complex with an alkoxyl substituent is amphiphilic and can be fabricated into LB films.[47] To manifest whether this is the case for the dinuclear complex, the isotherm study on **1** and **2** have been carried out. It was found that LB film preparation of **1** was unsuccessful even with the addition of stearic acid; while complex **2** could be successfully deposited on hydrophilic glass substrate without the addition of stearic acid.

Fig. 8 shows the isotherm for the dichloromethane solution of **2** spread on water subphase. The observed isotherm is reproducible. The surface pressure at which the monolayer collapse is *ca.* 57 mN m^{-1}, which is higher than that of the corresponding mononuclear platinum chloride complex with the alkoxyl substituent, *i.e.* 44 mN m^{-1}.[47] The higher collapse pressure of the dinuclear complex indicates expanded monolayer formation. Since the difference is approximately 13 mN m^{-1}, it is also indicative of a more '*side-on*' arrangement compared to the mononuclear complex (Fig. 9). The isotherm starts to lift at a larger molecular area of 211 $Å^2$. The limiting molecular area obtained by extrapolating the steep portion of the isotherm to zero pressure was found to be *ca.* 164 $Å^2$, which is much smaller than the estimated molecular

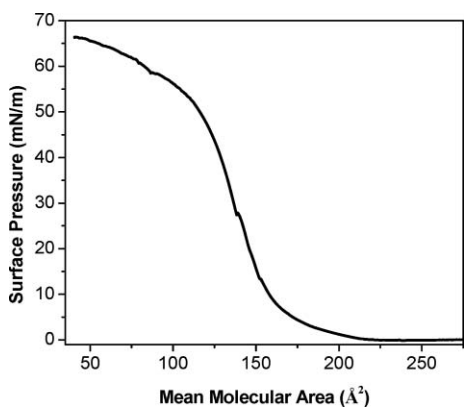

Fig. 8 Surface pressure–molecular area isotherm of **2**.

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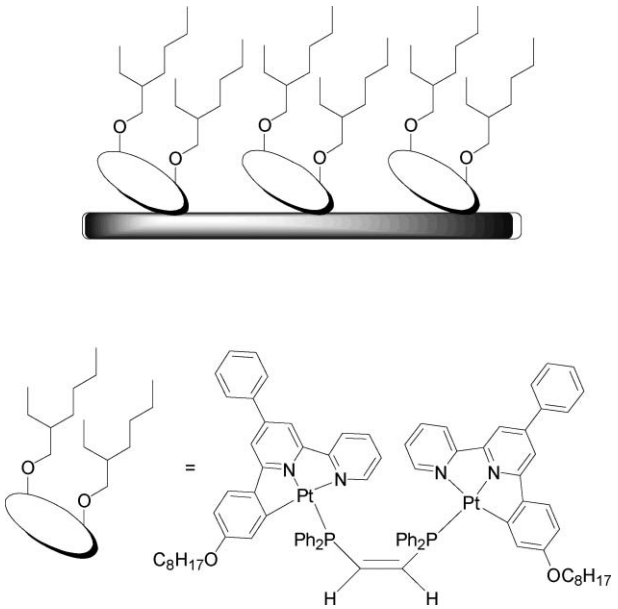

Fig. 9 Proposed molecular packing of **2** on air–water interface.

area (~644 Å^2). The tilt angle (θ) with respect to the interface normal is calculated to be ~14.7° using the equation $\sin\theta$ = limiting molecular area/calculated molecular area.

The surface morphology of the prepared LB films of **2** was studied using AFM technique. The images in Fig. 10 indicate a uniform and continuous film deposition. The light and dark regions represent the peaks and valleys on the surface, respectively. The grain-like structure observed in the images could be due to formation of aggregates. The 11 layer film (R_a (average roughness) = 1.392 nm) exhibits a higher roughness than that of the 5 layer (R_a = 0.760 nm) LB film, suggesting the growth of surface roughness with increased layers.

The UV-vis absorption spectra of **2** in CH_3CN solution and in 11 layer LB film are shown in Fig. 11. They all exhibit the similar feature, with a strong absorption band in the UV region that is assigned to the intraligand (CˆNˆN) π,π* transition, and a broad, moderately intense ^{1}MLCT/^{1}ILCT band in the visible region. However, the UV band in the LB film is ~18 nm bathochromically shifted compared to that observed in solution. The red-shift of the absorption band at ~322 nm suggests the presence of weak intermolecular π–π interactions.[60]

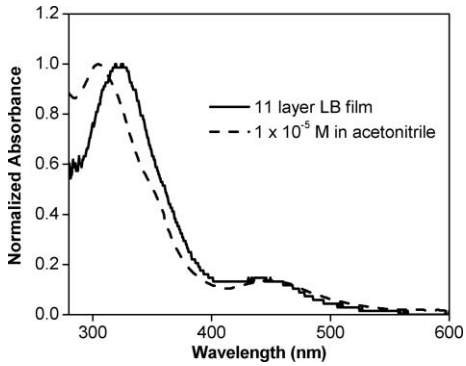

Fig. 11 UV-vis absorption spectra of **2** in CH_3CN solution and in LB film.

Emission was observed in the 5 layer and 11 layer LB films at room temperature. As shown in Fig. 12, the emission from the 5 layer and 11 layer LB films appears at *ca.* 600 nm, and the emission lifetime (~2.5 μs) is comparable to that in solution at room temperature, indicating the same emitting state as that in solution. Neither the lifetime nor the emission energy changes with increased number of layers in LB films. These observations suggest that no intermolecular Pt–Pt interactions that would influence the emission energy occur in the LB films even though slight aggregation was observed from the AFM images of the LB films.

Vapochromic effect of 1

In the past, vapochromic effect of many mononuclear platinum polypyridine complexes has been reported.[34,35,44,61–64] However, reports on the vapochromic effect of dinuclear platinum complexes are scarce. Che *et al.* reported the vapochromic behavior of $(C\hat{N}\hat{N}C)_2Pt_2(\mu\text{-dppm})$ (where CˆNˆC denotes 2,6-di-(2′-naphthyl)-4-phenylpyridine), which changes color from yellow to bright orange upon exposure to $CHCl_3$–CH_2Cl_2.[44] The vapochromic effect was attributed to the presence of accessible solvent channels of right size/shape in the crystal packing. Because of the rigid structure of the dinuclear complexes **1** and **2**, it is possible that they would form appropriate solvent channel in the crystal form as well and thus exhibit vapochromic effect. To demonstrate this, the vapochromic effect of these two dinuclear platinum complexes is investigated by deposition of these complexes on filter paper and exposure of the filter papers to a number of volatile organic compounds (VOC's).

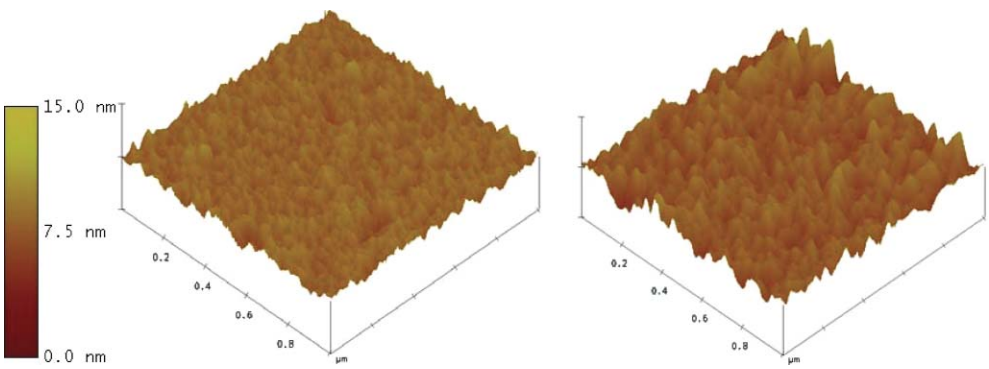

Fig. 10 AFM images of 5 layer (left) and 11 layer (right) LB films of **2** at scanning height of 15 nm and scanning area of 1 μm × 1 μm.

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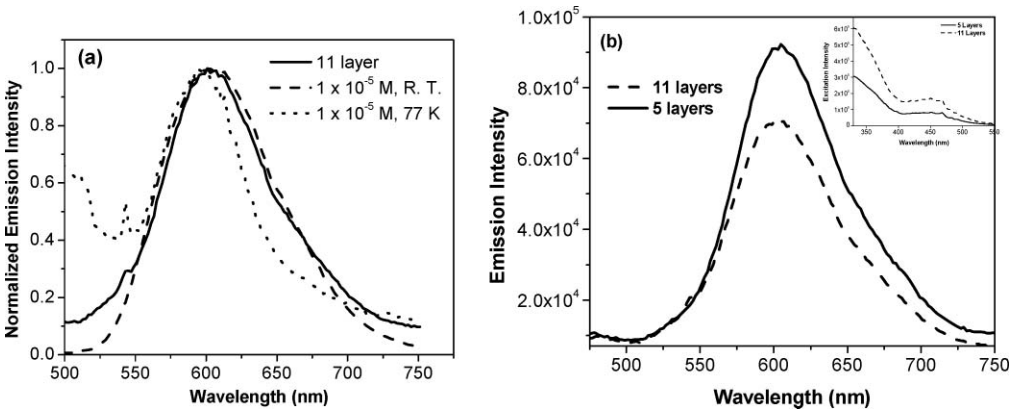

Fig. 12 Emission spectra of **2** (a) in acetonitrile and LB film, (b) LB film with different layers (λ_{ex} = 445 nm). Inset: Excitation spectra monitored at λ_{em} = 600 nm.

Our results show that only **1** shows vapochromic behavior when exposed to heteroatom-containing organic vapors, such as ether, ethanol, dichloromethane, chloroform, ethyl acetate, tetrahydrofuran and acetonitrile *etc*. Upon exposure to VOC's, the color of the filter paper changes from the initial yellow color to deep red (Fig. 13). The vapochromic behavior was reversible. Upon leaving the deep-red filter paper to atmosphere for 10–15 min or by heating the filter paper changes back to its initial yellow color. With reference to the work reported by Che *et al.* for the dinuclear [(C^N^C)$_2$Pt$_2$(μ-dppm)] complex,[44] the vapochromic behavior of **1** could possibly be rationalized by the weak non-covalent complex–complex, complex–solvent and solvent–solvent interactions[44] in **1** when the heteroatom-containing solvent vapors are trapped in the crystal lattice. In contrast, complex **2** does not exhibit any vapochromic effect to any of the VOC's tested. This could possibly be related to the presence of the branched alkoxyl chain, which would prevent the aforementioned non-covalent interactions. To better understand the vapochromic behavior of **1**, it is important to study the single-crystal structures of **1** in the presence and absence of VOC's. Unfortunately, all of our attempts to grow single crystal of **1** have failed to date. Therefore, a full explanation of the observed vapochromic effect is not possible at this time.

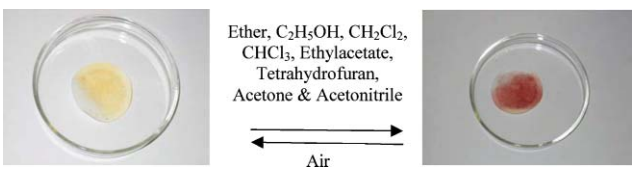

Fig. 13 Vapochromic response of **1** towards VOCs.

Conclusion

Dinuclear Pt(II) C^N^N complexes **1** and **2** with rigid bridging ligand were synthesized and their photophysical properties were systematically investigated. Unlike the dinuclear platinum C^N^N complex with the flexible diphenylphosphinoethane bridging ligand, the rigid bridging ligand in **1** and **2** prevents the conformational variation at different concentrations. The presence of alkoxyl substituent on the diphenylbipyridine ligand shifts the lowest-energy absorption and emission band to a longer wavelength, presumably due to the involvement of the ILCT character into the lowest excited states. The introduction of the alkoxyl substituent also makes **2** amphiphilic, thus LB films were prepared for **2**. The excited-state characteristics of **2** in LB films are quite similar to those in solutions. In addition, **1** displays reversible vapochromic behavior to heteroatom-containing VOC's.

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