Synthesis and spectroscopic properties of modular platinum(II) terpyridine phosphorescent pockets[†]

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Received 6th January 2009, Accepted 27th March 2009 First published as an Advance Article on the web 29th April 2009 DOI: 10.1039/b900030e

A modular design approach has been utilized to develop molecular 'pockets' featuring three integrated components, namely a phosphorescent Pt(II)- π (organic) moiety, a suitable receptor group, and a rigid, conjugated connecting backbone, and the cavities therein are examined by NMR spectroscopy and an X-ray crystal structure. Their photophysical properties have been investigated; unusually for Pt-terpyridine derivatives, the complexes are luminescent (near-red ³MLCT emission) in solution at room temperature. It has been shown that their emissive characteristics are affected by the nature of the backbone component but not the receptor group.

Introduction

The design of fluorescent and colorimetric sensors for anionic analytes has employed approaches based on molecular recognition and supramolecular chemistry.¹ While organic hosts have been investigated intensively, the development of transition metalorganic systems can offer distinct advantages including visiblelight signalling, inherent electrostatic attraction, good tunability, and well-defined structures and coordination geometries with potential binding sites.² For example, the versatile indicator

† Electronic supplementary information (ESI) available: Experimental details and characterization data for functionalized terpyridine ligands and 1–4; 77 K glass and solid-state emission data for 1–4; absorption and solution emission spectra of 1 and 2 in CH_2Cl_2 and CH_3CN at 298 K. CCDC reference number 716277 for 2[ClO₄]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b900030e

displacement assay approach pioneered by Anslyn *et al.*³ has been highly successful.⁴ We deemed that the pursuit of integrated phosphorescent molecular hosts which reversibly utilize noncovalent interactions would be desirable, and proceeded to devise a modular-based design strategy encompassing the following chemical and structural features: 1) a coordinatively unsaturated transition metal-(π -organic) phosphorescent signalling/sensing unit, enabling axial substrate-binding interactions and visible-light reporting without interference from organic/background fluorescence; 2) a receptor component displaying complementarity with intended guest(s), linked to the luminophore by a rigid backbone to maintain structural integrity; 3) conjugated units for improved communication between modules; 4) a robust framework that is easy to functionalize (Scheme 1).

Pt(II)-oligopyridine moieties are ideally suited as luminophores in this strategy because of their ability to exhibit diverse and tunable excited states that are exceptionally sensitive to perturbations in the surrounding micro-environment.^{5,6} In this study, the cationic Pt-terpyridine (tpy) moiety is expected to facilitate anion-binding, although the charge should not be localized,



Scheme 1 Modular design of phosphorescent pockets.

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thus reducing unfavourable solvation effects. In addition, the associated near-red emission can help to minimize background interference in sensing applications. This would cumulate in the creation of a ditopic phosphorescent pocket, which may display interesting binding properties and selectivity. Unusually, the Pt-terpyridine complexes in this work are emissive in solution at room temperature.

Results and discussion

Synthesis and NMR characterization

A modular synthetic methodology has been developed for this series of Pt(II) complexes. Starting from a rigid backbone unit such as xanthene⁷ or dibenzofuran⁸ (Scheme 2), the attachment and integration of any chosen luminophore and receptor group can be readily achieved by Pd-coupling reactions, and has been demonstrated for Pt-tpy and benzoic acid/benzoate/diaminotriazine respectively. Hence, new Pt(II) molecular 'pockets' bearing these modules have been prepared in order to examine the impact of cavity size and receptor group upon luminescent properties and ultimately, sensing capabilities (1-4, Scheme 1). Bulky substituents on the backbone are incorporated to impede intermolecular π -stacking and related aggregation processes, which may complicate future sensing studies. As may be anticipated, the solubility of 1 and 4 is poor in non-polar organic solvents but improved in polar media, rendering them suitable for polar and possibly aqueous applications.

It is intriguing to note that during the synthesis of the Cl⁻, ClO₄⁻ and PF₆⁻ salts of **2**, substantial ¹H NMR perturbations were observed for the aryl hydrogens H_d, H_e and H_f in the cavity (Fig. 1a: relative to Cl⁻ in CD₂Cl₂, Δ ppm = -0.54, -0.52 and -0.24 for ClO₄⁻; -0.67, -0.61 and -0.33 for PF₆⁻ respectively). Furthermore, we have shown that by using **2**[Cl] as a prototypical anion sensor, the qualitative NMR discrimination of anions is feasible (Fig. 1b). Loeb and co-workers have used ¹H NMR titrations to investigate a [Pt(urea-isoquinoline)₄]²⁺ receptor, which employs urea hydrogen-bond donors to encapsulate anions in solution,⁹ while analogous organic systems have been reported.¹⁰ It is generally known that conventional ion-pairing contacts in solution can alter the structure/conformation and generally cause ¹H NMR signals to shift. Here, since only specific protons in the cavity (H_{d-f}) are greatly affected and the majority are undisturbed, we propose that the unusual NMR perturbations for different anions may also be attributed to weak C–H…X⁻ or π -anion¹¹ interactions with the said aryl protons (see next section).

Crystal structure

The molecular structure of $2[ClO_4]$ has been determined by X-ray crystallography (Fig. 2).12 The xanthene backbone is slightly puckered as expected, and dihedral angles of ca. 58 and 38° with the central pyridine and benzoate rings respectively are observed. Importantly, a dihedral angle of 0.6° is evident between the Pttpy and benzoate planes, demonstrating that these fragments are rotated to approach coplanarity. This conformation enables them to be sufficiently close to maximize intramolecular edge-to-edge π - π interactions (interplanar separations *ca.* 3.5 Å; *e.g.* $C(6) \cdots C(33)$ and $C(7) \cdots C(34)$ of 3.54 and 3.52 Å respectively), and changing the afore-mentioned dihedral angles would presumably reduce the π -overlap. While Pt \cdots O(ester) contacts are not detected, weak C-H... anion interactions are found at the cavity/tpy unit. The shortest $C-H \cdots OClO_3^-$ separation of 2.7 Å $(C \cdots O 3.4 \text{ Å}; C-H \cdots O 132^{\circ})$ is observed at H(4), which corresponds to the aryl hydrogen H_d in the cavity (see above). Nevertheless, the $C-H \cdots ClO_4^-$ interactions in this structure are relatively weak, and this may be attributed to crystal packing effects.

Absorption and emission spectroscopy

The photophysical properties of 1-4 [ClO₄] have been investigated (Table 1). The UV-vis absorption spectra display similar patterns,



Scheme 2 Synthesis of dibenzofuran-linked complex 4.



Fig. 1 (a) Aromatic region in ¹H NMR spectra (300 MHz, CD_2Cl_2 , 298 K) of **2**[X]. (b) Aromatic region in ¹H NMR spectra (300 MHz, $CDCl_3$, 298 K; * = solvent satellites) of **2**[Cl] (1 × 10⁻³ M) upon addition of 0.25 equivalents of anions (^aBu₄N⁺ salts).

with intense bands at <350 nm ($\varepsilon > 1 \times 10^4$ dm³ mol⁻¹ cm⁻¹) which closely resemble those of the respective non-metallated ligand in terms of the structured nature and large extinction coefficients, plus a low-energy band at $\lambda_{max} \sim 410$ nm of moderate intensity ($\varepsilon > 4000$ dm³ mol⁻¹ cm⁻¹) that is absent from the ligand precursor. As reported in spectroscopic studies of related Pt(II)tpy complexes,^{13,14} the high-energy bands at < 350 nm are assigned as the intraligand $\pi\pi^*$ transitions of the aryl and tpy groups, whereas the absorption at $\lambda_{max} \sim 410$ nm is assigned as spin-allowed MLCT ¹[(5d)Pt $\rightarrow \pi^*$ (tpy)]. The similarity between the absorption spectra of **1–3** suggests that the change from benzoate to acid and triazine results in minimal differences in the charge transfer nature of the complexes.

The parent terpyridine-Pt(II) complex is non-emissive in solution at room temperature,¹³ but judicious substitution, especially at the tpy moiety, can yield appreciably emissive derivatives.¹⁴ In this work, the xanthene complexes **1–3** are luminescent in solution at room temperature (Table 1 and Fig. 3 for **1**; see ESI† for 77 K glassy and solid-state emissive data). The excitation spectra obtained closely resemble the corresponding absorption



Fig. 2 Perspective views of $2[ClO_4]$ (hydrogen atoms are omitted for clarity; top: 30% probability ellipsoids; bottom: coplanarity of tpy and benzoate groups, and position of perchlorate anion).

Table 1 Photophysical data at 298 K a

Complex	UV-vis λ_{max}/nm ($\varepsilon \times 10^4/dm^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	Fluid emission $\lambda_{\max}/\operatorname{nm}(\tau/\operatorname{ns}; \Phi)$
1 [ClO ₄]	257 (4.44), 306 (2.06), 333 (1.31), 415 (0.422)	612 (30; 2.5 × 10 ⁻³)
2 [ClO ₄]	257 (5.67), 281 (3.60), 308 (2.34), 331 (1.81), 415 (0.557)	$617 (39; 2.5 \times 10^{-3})$
3 [ClO ₄]	257 (3.40), 283 (2.36), 337 (1.13), 412 (0.463)	607 (28; 2.2×10^{-3})
4 [ClO ₄]	263 (5.18), 340 (1.51), 359 (1.14), 389 (0.833), 406 (0.748) ^b	<i>b</i> , <i>c</i>

spectral bands, especially around λ_{max} 410 nm. The respective orange emission, lifetime and Stokes shift for 1–3 are entirely consistent with a ³MLCT excited state, as has been assigned for analogous Pt-tpy complexes.¹⁴ Conventional solvatochromic shifts for the absorption and solution emission bands of 1 and



Fig. 3 Absorption (298 K, CH₂Cl₂) and 298 K (CH₂Cl₂: blue) and 77 K (MeOH:EtOH [1:4]: green) fluid emission (λ_{ex} 410 nm) spectra of **1**[ClO₄] (10⁻⁵ M).

2 in CH₂Cl₂ and CH₃CN at 298 K have been observed (see ESI[†]). Estimated radiative decay rate constants $(k_r = \Phi_o/\tau_o)$ assuming $\Phi_{isc} = 1$) of *ca.* 83000, 64000 and 76000 are calculated for 1-3 respectively. Values of 10^3 - 10^5 for k_r indicate the heavy metal effect and are consistent with the forbidden nature of the triplet excited state. Like the absorption data, the comparable emission energies, lifetime and quantum yields signify that the receptor group does not significantly alter the excited state in this series. Unlike the ¹H NMR and solid-state emission data, the Cl⁻, ClO₄⁻ and PF₆⁻ salts of **2** afford identical ³MLCT emission at λ_{max} 580 nm in CH₂Cl₂ at 298 K (see ESI[†]), indicating that the impact of counterions upon the excited state in solution is negligible. In contrast to 1-3, the emission of the dibenzofuran analogue 4, which is reasonably soluble in polar solvents such as methanol and DMSO, is extremely weak possibly due to enhanced solvent quenching¹⁵ in the enlarged cavity. This would impose limitations on subsequent sensing studies, and demonstrates that the nature/size of the cavity in these complexes can affect their emissive properties.

These complexes generally exhibit 77-K glassy emissions that are blue-shifted from the respective solution emission at 298 K. For example, the glassy emission of 2[ClO₄] in butyronitrile at 77 K features a structured band at λ_{max} 520 nm with a vibronic progression of ~1200 cm⁻¹ (assigned as metal-perturbed intraligand), plus an additional low-energy band at λ_{max} 610 nm (Fig. 4) which begins to appear at 10⁻⁴ M and becomes more intense at higher concentrations. The energy and broad bandshape of this feature do not correspond to an additional vibronic structure. Moreover, while the vibronic emission band displays a lifetime of 35 µs at 520 nm, monitoring of the emission at 610 nm yielded a second-order exponential decay ($\tau_1 = 3.4, \tau_2 =$ 41 μ s), indicating the presence of two emitting species. Hence the concentration-dependent 610 nm band is tentatively assigned to excimeric emission.^{13,14d,16} The recrystallization of the Cl⁻, ClO₄⁻ and PF_6^- salts of 2 by diffusion of diethyl ether into CH_3CN give vellow, vellow-orange and orange crystalline solids respectively. A comparison of their solid-state emission spectra at 298 K (Fig. 5) revealed red-shifted emission maxima for larger anions, which is attributed to differences in intermolecular π -stacking and aggregation rather than C-H...anion contacts. The solid-state



Fig. 4 Normalized 77-K glassy emission spectra of $2[ClO_4]$ in butyronitrile at different concentrations (λ_{ex} 450 nm).



Fig. 5 Normalized solid-state emission spectra for Cl⁻ (red), ClO₄⁻ (black) and PF₆⁻ (green) salts of **2** at 298 K.

emissive properties of [Pt(tpy)Cl]⁺ salts and their relatives are known to be highly dependent on the counterion and solvent used for precipitation.^{13,17} As expected, the observed fluid and solidstate emission lifetimes are generally longer at low temperatures (see ESI⁺) as non-radiative processes become restricted.

Conclusion

Strategies to create modular Pt(II) terpyridine phosphorescent complexes, and tune the cavity size and receptor group/recognition capabilities in a rational manner, have been developed. Information regarding the nature of the cavity has been obtained by ¹H NMR and X-ray crystallography. The photophysical properties of the complexes have been examined using absorption and fluid emission spectra, and the modularity of the system has allowed us to illustrate that luminescent behaviour is affected by the size and nature of the cavity/backbone, but not the receptor component. Applications in phosphorescent sensing are under development.

Experimental

General considerations

All reactions were performed under a nitrogen atmosphere and solvents for syntheses (analytical grade) were used without further purification. Solvents for photophysical measurements were purified according to conventional methods. 'H NMR spectra were obtained on Bruker DRX 300 and 400 FT-NMR spectrometers (ppm) using Me₄Si as internal standard. ESI mass spectra were measured on a Perkin-Elmer Sciex API 365 mass spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer. Elemental analyses were performed on an Elementar Analysensysteme GmbH Vario EL elemental analyzer. UV-vis absorption spectra were obtained on an Agilent 8453 diode array spectrophotometer.

Steady-state emission spectra were recorded on a SPEX FluoroLog 3-TCSPC spectrophotometer equipped with a Hamamatsu R928 PMT detector, and emission lifetime measurements were conducted using NanoLed sources in the fast MCS mode and checked using the TCSPC mode. Sample and standard solutions were degassed with at least three freeze–pump–thaw cycles. Lowtemperature (77 K) emission spectra for glasses and solid-state samples were recorded in 5-mm diameter quartz tubes which were placed in a liquid nitrogen Dewar equipped with quartz windows.

The emission quantum yield was measured¹⁸ by using [Ru(bpy)₃](PF₆)₂ in degassed acetonitrile as the standard ($\Phi_r = 0.062$) and calculated by: $\Phi_s = \Phi_r (B_r/B_s)(n_s/n_r)^2 (D_s/D_r)$, where the subscripts s and r refer to sample and reference standard solution respectively, *n* is the refractive index of the solvents, *D* is the integrated intensity, and Φ is the luminescence quantum yield. The quantity *B* is calculated by the equation: $B = 1 - 10^{-AL}$; where *A* is the absorbance at the excitation wavelength and *L* is the optical path length. Errors for λ (±1 nm), τ (±10%), and Φ (±10%) are estimated.

Syntheses

Please see ESI[†] for full synthetic details.

1[ClO₄]. A mixture of K_2 PtCl₄ (0.017 g, 0.041 mmol) in water (0.5 mL) and the terpyridine-xanthene-benzoic acid ligand (0.043 g, 0.063 mmol) in CH₃CN/CH₂Cl₂ (3:1; 8 mL) was stirred under reflux for 48 h to give a yellow solution containing 1[Cl]. After cooling, the solution was mixed with saturated NaClO₄ in MeOH. After removal of volatiles, the mixture was re-suspended in CH₂Cl₂, then filtered, and the filtrate was dried in vacuo to afford 1[ClO₄] as a yellow solid. Recrystallization by vapour diffusion of diethyl ether into a DMF/DMSO mixture afforded a yellow crystalline solid (yield: 65%). Found: C, 53.65; H, 4.61; N, 4.39. Calc. for C₄₅H₄₃N₃O₇Cl₂Pt (1003.83): C, 53.84; H, 4.32; N, 4.19. IR (KBr, cm⁻¹): 1701, 1609. ¹H NMR (300 MHz, CD₃OD): δ 8.96 (d, J = 5.2 Hz, 2H), 8.40 (s, 2H), 8.29 (t, J = 7.5 Hz, 2H), 8.19 (d,J = 7.5 Hz, 2H), 7.84–7.80 (m, 2H), 7.80 (d, J = 2.3 Hz, 1H), 7.62 (d, J = 2.3 Hz, 1H), 7.61 (d, J = 2.3 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 2.3 Hz, 1H), 1.81 (s, 6H), 1.46 (s, 9H), 1.36 (s, 9H). ES-MS (+ve mode): m/z 904 [M⁺].

 $2[CIO_4]$. The procedure for $1[CIO_4]$ was adopted using the terpyridine-xanthene-benzoate ligand. Recrystallization by vapour diffusion of diethyl ether into a CH_2Cl_2 solution afforded

yellow crystals (yield: 68%), one of which was used for X-ray crystal analysis. Found: C, 53.17; H, 4.53; N, 4.28. Calc. for C₄₆H₄₅N₃O₇Cl₂Pt·H₂O (1035.99): C, 53.34; H, 4.57; N, 4.06. IR (KBr, cm⁻¹): 1718, 1609. ¹H NMR (300 MHz, CD₂Cl₂): δ 9.11 (d, J = 5.6 Hz, 2H), 8.32-8.26 (m, 2H), 8.14 (s, 2H), 8.00 (d, J = 7.6 Hz, 2H), 7.81 (t, J = 6.2 Hz, 2H), 7.72 (d, J = 2.2 Hz, 1H), 7.55 (d, J = 2.3 Hz, 1H), 7.52 (d, J = 2.2 Hz, 1H), 7.44 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 2.3 Hz, 1H), 3.91 (s, 3H), 1.81 (s, 6H), 1.44 (s, 9H), 1.36 (s, 9H). ES-MS (+ve mode): m/z 918 [M⁺].

3[CIO₄]. The procedure for **1**[CIO₄] was adopted using the terpyridine-xanthene-diaminotriazine ligand. Recrystallization by vapour diffusion of diethyl ether into a CH₃CN solution afforded yellow crystals (yield: 63%). Found: C, 49.76; H, 4.41; N, 11.02. Calc. for C₄₁H₄₂N₈O₅Cl₂Pt (992.81): C, 49.60; H, 4.26; N, 11.29. IR (KBr, cm⁻¹): 1638, 1618. ¹H NMR (CD₂Cl₂ and CD₃OD, 300 MHz) δ 9.17 (d, 2H), 8.38–8.30 (m, 2H), 8.25 (s, 2H), 8.10–8.06 (d, 2H), 7.86–7.78 (m, 2H), 7.72 (s, 1H), 7.63 (s, 1H), 7.51 (s, 1H), 7.44 (s, 1H), 1.78 (s, 6H), 1.43 (s, 9H), 1.37 (s, 9H). ES-MS (+ve mode): *m/z* 893 [M⁺].

4[ClO₄]. A mixture of K_2 PtCl₄ (0.011 g, 0.0258 mmol) in DI water (2 mL) and the terpyridine-dibenzofuran-benzoic acid ligand (0.017 g, 0.0258 mmol) in CH₃CN/CH₂Cl₂ (4 mL) was stirred under reflux for 24 h to give a yellow suspension. After the removal of volatiles, the yellow solid was dissolved in CH₃CN/CH₂Cl₂, filtered into saturated LiClO₄ in MeOH, and the yellow solution was washed with DI water. After removal of solvents, the product was obtained by washing copiously with diethyl ether to yield an orange solid (0.010 g, 40%). Found: C, 48.61; H, 3.97; N, 4.14. Calc. for C₄₀H₃₇N₃O₇Cl₂Si₂Pt (993.89): C, 48.34; H, 3.75; N, 4.23. IR (KBr, cm⁻¹): 1701, 1609. ¹H NMR (300 MHz, d_6 -DMSO): δ 9.17 (s, 2H), 8.76 (s, 1H), 8.72 (d, J =4.7 Hz, 2H), 8.65 (d, J = 7.9 Hz, 2H), 8.61 (s, 1H), 8.47 (t, J =7.9 Hz, 1H), 8.20 (d, J = 8.5 Hz, 2H), 8.17 (s, 1H), 7.94 (d, J =8.2 Hz, 2H), 7.91 (s, 1H), 7.87-7.83 (m, 2H), 7.71-7.69 (m, 1H), 0.50 (s, 9H), 0.46 (s, 9H). ES-MS (+ve mode): m/z 894 [M⁺].

Acknowledgements

The work described in this paper was fully supported by grants from the Research Grants Council of the Hong Kong Special Administrative Region, China (CityU 100405) and City University of Hong Kong (7001787).

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- 12 X-ray diffraction data were collected on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatised Mo-K_a radiation ($\lambda = 0.71073$ Å). Selected crystal data for **2**[ClO₄]: C₄₆H₄₅N₃O₇Cl₂Pt, $M_w = 1017.84$, monoclinic, P_{2_1}/c , a = 21.261(7), b = 12.008(4), c = 21.963(7) Å, $\beta = 113.71(3)^\circ$, V = 5134(3) Å³, Z = 4, T = 293(2) K, $D_c = 1.317$ g cm⁻³, μ (Mo K_a) = 2.883 mm⁻¹, F(000) = 2040, $2\theta_{max} = 51.4^\circ$, 9693 independent reflections ($R_{int} = 0.1083$), 477 variable parameters, $R_1 = 0.081$ [$I > 2\sigma(I)$], w $R_2 = 0.189$. During refinement, the methyl groups on xanthene are found to be disordered. In the final stage of least-squares refinement, the disordered C atoms, plus the N atoms around Pt atom were refined isotropically, and other non-hydrogen atoms were refined anisotropically. Due to the marginal data quality, only general conclusions regarding the structure are drawn.
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