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# Congested Cyclometalated Platinum(II) Ditopic Frameworks and Their Phosphorescent Responses to S-Containing Amino Acids

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New phosphorescent platinum(II) molecular hosts featuring a tridentate N,C,N-coordinating ligand, a conformationally rigid organic linker, and a binding group have been prepared. The complexes have been fully characterized by various spectroscopic techniques, and the X-ray crystal structure of one derivative has been determined. Their photophysical properties have been studied, and intense green metal-perturbed $^3$IL emission is observed in solution at room temperature. The luminescent responses of these Pt(II) hosts to amino acids have been investigated: emission quenching and UV−vis absorption changes in polar/aqueous media are detected for terminal thiols only, and unusual preferential binding is apparent for cysteine over homocysteine. The nature of the host−guest interactions has been examined by quantitative and comparative binding studies, mass spectrometry, and DFT calculations, which indicate that these observations may be ascribed to the presence of rigidly positioned ditopic binding sites.

## Introduction

Interest in the development of luminescent and colorimetric sensors and probes continues unabated.[1] Design strategies evolved from molecular phenomena, such as rigidification and restricted rotation and conformation, have been explored for fluorescent sensing applications.[2] While the focus on organic hosts has been more acute, it is evident that transition metal-based systems can engender advantages such as tunable, well-defined coordination geometries and visible light signaling, as well as alternative binding interactions and pathways. Our current studies are directed toward the modular[3] synthesis of crowded molecular hosts and frameworks featuring environmentally sensitive platinum(II) luminophores, which have been conceived to afford unusual photophysical characteristics and the possibility of controlling molecular conformations, as well as allow the reporting of molecular-level perturbations and events.[4]

Here, we describe the synthesis and photophysical properties of phosphorescent host complexes containing the cyclometalated [N,C,N-Pt(II)] [N,C,N = 2,6-di(2′-pyridyl)(σ-aryl)] moiety and a potential binding site, which are rigidly linked by a xanthene moiety to yield shape-persistent cavities that only permit axial rotation of the respective components. Square-planar polypyridyl[5] and cyclometalated[6,7] Pt(II) complexes and multinuclear assemblies have been extensively studied over the past three decades, owing to their tendency to undergo interplanar stacking and metal−metal interactions and for their diverse excited-state properties. In particular, their open geometry facilitates the observation of

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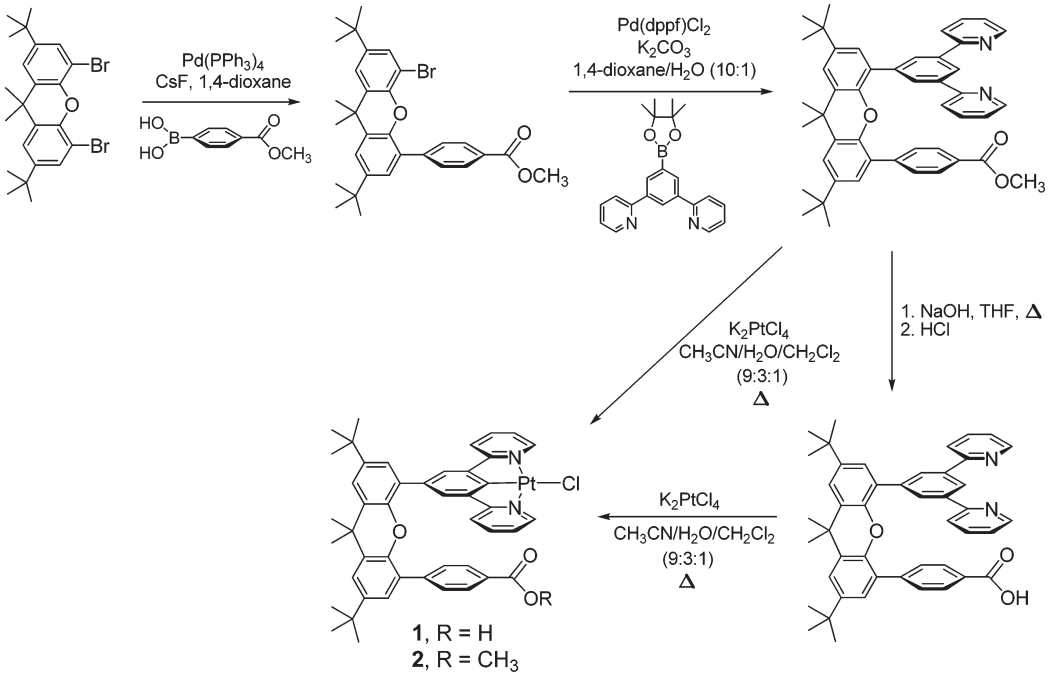
**Scheme 1. Synthesis of Complexes 1 and 2**




low-energy deep red fluid emissions (ascribed to metal−metal-to-ligand charge transfer, MMLCT [d$\sigma$*→$\pi$*] transitions), which are highly responsive to changes in the immediate microenvironment.[8] The highly emissive [N,C,N-Pt(II)] luminophore, which was developed by Williams and has attracted attention in material applications,[9] was chosen for this work because it is well established that the ancillary Cl ligand in tridentate polypyridyl-Pt(II) complexes may be labile and can undergo displacement reactions with S- and N-donors,[10] and this is particularly true for [Pt(N,C,N)Cl] derivatives due to the strong trans effect of the $\sigma$-aryl donor.[11] We therefore proposed to exploit this lability, since such substitution reactions should be accompanied by photophysical perturbations. Hence, ditopic hosts featuring one binding moiety plus an accessible and reactive Pt(II) module (positioned directly in the cavity to augment sensitivity) have been targeted, while the associated rigidity may confer selectivity upon substrate binding.

In this study, although the phosphorescent Pt(II) frameworks display limited aqueous solubility, interesting selectivity is observed in polar/aqueous media for aminothiols over standard amino acids, and preferential binding is unusually detected for cysteine (Cys) over homocysteine (Hcy). While the sensing media used are not biocompatible, these observations demonstrate the potential viability of the present design approach using crowded ditopic phosphorescent hosts. Reports of binuclear Pt(II) complexes supported by a xanthene backbone have appeared in the literature.[4b,9d,12]

## Results and Discussion

**Synthesis and Characterization.** The conformationally rigid complexes **1** and **2** (Scheme 1) are prepared from the substituted 4,5-dibromoxanthene precursor by Pd-catalyzed coupling reactions at elevated temperatures to give the corresponding ligands, followed by treatment with $K_2PtCl_4$. The benzoic acid group is incorporated as a potential binding unit (with ester as control), and the xanthene fragment acts as a robust and readily functionalizable backbone that links the luminophore and binding sites. The *tert*-butyl groups afford good solubility in nonpolar organic solvents such as $CH_2Cl_2$ and $CH_3CN$ by impeding $\pi$-stacking aggregation processes. However, like the cationic terpyridine analogue,[3] complex **1** displays limited aqueous solubility.

Complexes **1** and **2** have been fully characterized by $^1H$ and $^{13}C$ NMR spectroscopy and ESI-MS, the latter showing a peak cluster that corresponds closely to the respective calculated isotopic pattern (Supporting Information). The molecular structure of **2** has been determined by X-ray crystallography (Figure 1).[13] The Pt center resides in a distorted square-planar geometry, and the Pt−C(aryl) bond

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(13) Crystal data for **2** ($\lambda$ = 0.71073 Å): $C_{47}H_{45}N_2O_3ClPt$, fw = 916.40, monoclinic, $P2_1/c$, $a$ = 19.017(5) Å, $b$ = 18.540(4) Å, $c$ = 11.446(5) Å, $\beta$ = 97.232(3)°, crystal size 0.2 × 0.2 × 0.2 mm$^3$, $V$ = 4003.6(2) Å$^3$, $Z$ = 4, $D_c$ = 1.520 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 3.615 mm$^{-1}$, $F$(000) = 1840, $T$ = 293(2) K, $2\theta_{max}$ = 50.0°, 7032 indep reflns ($R_{int}$ = 0.0408), 496 variable parameters, $R_1$ = 0.0263 [$I > 2\sigma(I)$], $wR_2$ = 0.0491, GOF($F^2$) = 0.932, largest diff peak/hole = 0.637/−0.554 e Å$^{-3}$.

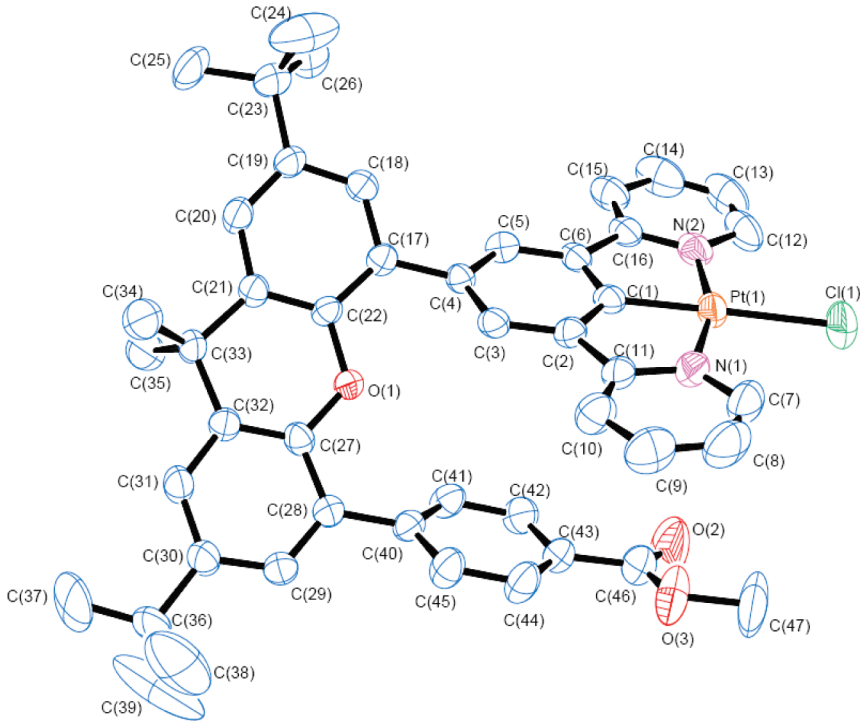


**Figure 1.** Perspective view of **2** (50% probability ellipsoids; hydrogen atoms omitted for clarity).

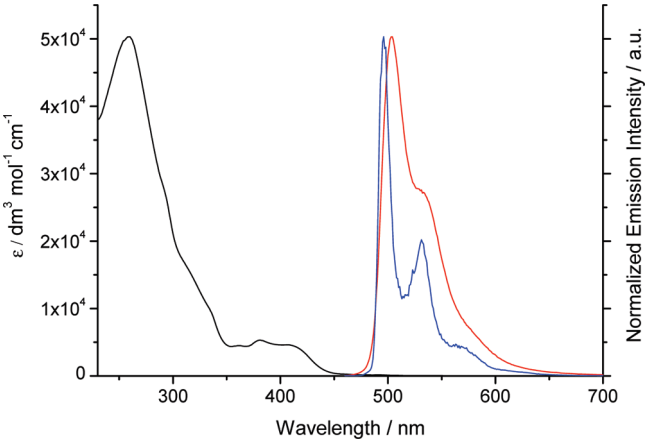


**Figure 2.** UV−vis absorption (black) and fluid emission (red; $\lambda_{ex}$ 408 nm) spectra at 298 K ($10^{-5}$ M in $CH_3CN$) and 77 K emission spectrum (blue; $10^{-3}$ M in $^n$BuCN; $\lambda_{ex}$ 408 nm) of **1**.

is noticeably shorter than the Pt−N(py) bonds [Pt(1)−C(1) 1.897(3), Pt(1)−N(1) 2.046(3), Pt(1)−N(2) 2.045(3) Å].[9a,b] The xanthene group is slightly puckered as expected, and dihedral angles of 49° and 47° with the [N,C,N] and benzoate rings, respectively, are observed. A dihedral angle of 9.7° between the rigid [N,C,N] and benzoate fragments is inconsistent with the presence of $\pi-\pi$ interactions, even though interplanar separations down to 3.53 Å are apparent, and crystal packing effects may therefore be more dominant in determining the molecular conformation in **2**.

**Photophysical Properties.** The UV−vis absorption and fluid emission data for complexes **1** (Figure 2) and **2** are very similar (Table 1). Namely, intense absorption bands at $< \lambda_{max}$ 330 nm ($\varepsilon > 1 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$) are assigned to $^1(\pi-\pi^*)$ transitions, and moderately strong absorption bands at $\lambda_{max}$ 360−410 nm ($\varepsilon \approx 4000-5000$ dm$^3$ mol$^{-1}$ cm$^{-1}$) are attributed to spin-allowed transitions with significant charge transfer character involving Pt(II) (i.e., $^1$MLCT), in accordance with previous reports for analogous aryl-substituted [Pt(N,C,N)Cl] complexes.[9] The highly structured green emission ($\lambda_{max}$ 504 nm; vibronic progression ≈ 1080 cm$^{-1}$) observed for both **1** and **2** at 298 K in $CH_3CN$ is attributed to a Pt-perturbed $^3(\pi-\pi^*)$ excited state, and high quantum yields ($\Phi \approx 60\%$ in degassed $CH_3CN$) are obtained. The shift for the emission maxima in 77 K $^n$BuCN glass is minimal, consistent with the predominantly ligand-centered nature of the excited state.

In contrast to previous observations for cationic terpyridine-Pt congeners[3] and [N,C,N-Pt] derivatives,[9b] excimeric emission was not observed for **1** and **2** for concentrations up to $10^{-3}$ M in 77 K $^n$BuCN glass or DMF/$H_2O$ mixtures at 298 K. This is presumably due to the presence of the *tert*-butyl groups and is beneficial for sensing studies, since host aggregation and related complications should be circumvented. Minor variations for the solid-state emission maxima between **1** and **2** (Supporting Information) are attributed to different crystal-packing effects (strong hydrogen-bonding interactions are possible only in **1**). In general, the close resemblance between the absorption and emission spectra of **1** and **2** signifies that the change from benzoic acid to ester results in minimal differences in the charge-transfer transitions and excited states of these complexes, which originate from the [N,C,N-Pt(II)] moiety.

**Luminescent Response of Complex 1 to Amino Acids.** In order to investigate the nature of the proposed ditopic sites and the possibility of deriving selectivity for host systems such as **1**, binding studies with standard amino acids have been performed by spectrofluorometric titrations in aerated 1:1 $CH_3CN$/Tris buffer (pH 7.2) with 5% DMF (Figure 3).[14] The ionization of the acid group in complex **1** was probed by

(14) Tris buffer composition: tris(hydroxymethyl)aminomethane (0.1 M) and KCl (0.1 M) at pH 7.2. Precipitation was not observed during any of the titrations described.

**Table 1. Photophysical Data**[a]

| complex | UV−vis $\lambda_{max}$ ($\varepsilon \times 10^3$)[b] | 298 K fluid emission[b] $\lambda_{max}$ ($\tau$; $\Phi$) | 77 K glass emission[c] $\lambda_{max}$ ($\tau$) |
|---|---|---|---|
| **1** | 260 (50.3), 335 (9.62), 360 (4.48), 381 (5.31), 406 (4.62) | 504 (max), 533 (5.0; 0.63) | 497 (max), 531, 570 (8.1) |
| **2** | 260 (51.3), 335 (9.10), 361 (4.16), 382 (5.49), 409 (5.09) | 504 (max), 533 (5.9; 0.62) | 499 (max), 532, 572 (8.8) |

[a] $\lambda$ in nm; $\varepsilon$ in dm$^3$ mol$^{-1}$ cm$^{-1}$; $\lambda_{ex}$ 408 nm; lifetimes ($\tau$) in $\mu$s. [b] In degassed $CH_3CN$ ($10^{-5}$ M). [c] In $^n$BuCN ($10^{-3}$ M).

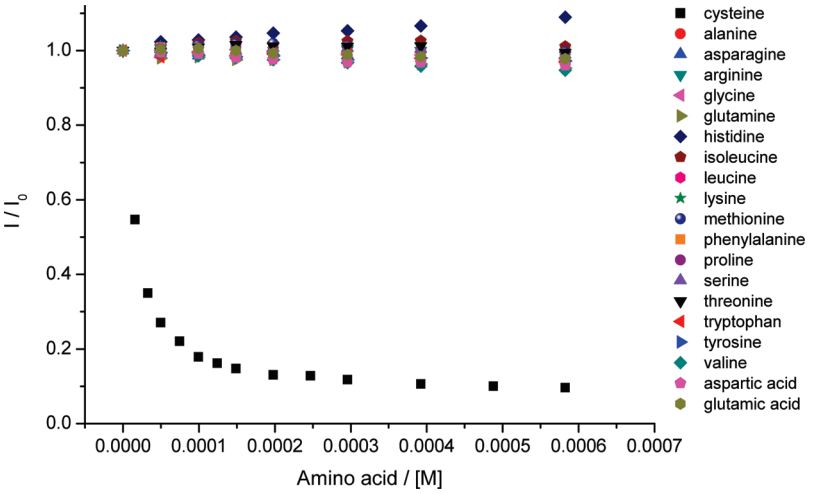


**Figure 3.** Binding isotherms for **1** ($5.0 \times 10^{-5}$ M) with amino acids in aerated 1:1 $CH_3CN$/Tris buffer (pH 7.2) with 5% DMF.

an acid−base titration experiment,[15] which indicated that the carboxylate moiety exists at neutral pH. Apparent p$K_a$ values ranging from 3.2 to 6.8 in organic/aqueous media have been reported for related (oligo)pyridyl-Pt(II) carboxylate derivatives.[8d,16] Saliently, substantial emission quenching and red-shifted UV−vis absorption bands for **1** are detected with cysteine only (see below for quantitative experiments),[17] which is tentatively ascribed to interaction/reaction with the −SH group (see Figure 4 and discussion). In this regard, the lack of response for methionine is consistent with the hindered lone pair and lower nucleophilicity for the −SMe unit. Competition experiments with standard amino acids have been conducted, indicating selectivity for cysteine (Supporting Information).

ESI mass spectrometry was used to probe the nature of the binding interaction (or reaction) between **1** and Cys. The dominant signal in the ESI mass spectrum (+ve mode) of the reaction mixture containing **1** and excess cysteine using zero declustering potential (Figure 4) is a cluster at $m/z = 1009.5$, which displays excellent agreement with the calculated isotopic pattern for the $[\mathbf{1} - Cl + Cys + Na]^+$ species. This provides evidence to support the expected chloride displacement and formation of the Pt−S(Cys) bond. At a declustering potential of 40 V, the cluster at $m/z = 1009.5$ persists, but the $[\mathbf{1} - Cl]^+$ species at $m/z = 866.5$ becomes more prominent (Supporting Information), implying that the Cl ligand is indeed labile and readily displaced under these conditions.

The facile reaction of thiols with Pt(II)−Cl bonds is well known, and literature reports concerning the characterization of Pt−S(cysteine)[18] and Pt−S(glutathione)[19] species and the binding of [Pt(N,C,N)Cl] to intracellular thiols[20] have appeared. In addition, several classes of oligopyridyl-Pt complexes ligated by amino acids have been described.[10,21] Following the results from ESI-MS, DFT calculations have been performed to optimize the structure of **1** (ionized; $Cl^-$ displaced) with $Cys^-$ (Supporting Information). The energy-minimized calculated (Gaussian) structure, which was confirmed to be a minimum from vibrational frequency calculations, represents a plausible binding mode in which the $Cys^-$ moiety chelates to the ditopic host through a Pt−S bond plus a charge-assisted hydrogen bond from the ammonium group to the $CO_2^-$ moiety (N−H$^+\cdots$O 1.546 Å). Nevertheless, we note that this gas-phase calculated structure may not represent an accurate model of the binding between **1** and Cys in the organic/aqueous media described, where solvent effects and competing interactions exist.

**Comparative Responses of Complexes 1 and 2 to Thiols: Preferential Binding to Cys over Hcy and Insight into Nature of Binding.** Quantitative spectrofluorometric titrations have been

(15) The pH change upon addition of 0.04 M NaOH(aq) to a 20 mL stock solution of **1** (50 $\mu$M) in a mixture of 10 mM HCl and 100 mM KCl(aq)/$CH_3CN$ (1:1 v/v) was monitored. The resultant pH change in the buffer region was small, and the apparent p$K_a$ was estimated to be ~5.5.

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(17) The buffer concentration is an important consideration, since partial enhancements ($I/I_0$ up to 1.2) for aspartic and glutamic acids are observed when very dilute buffer solutions (e.g., 0.005 M) are used.

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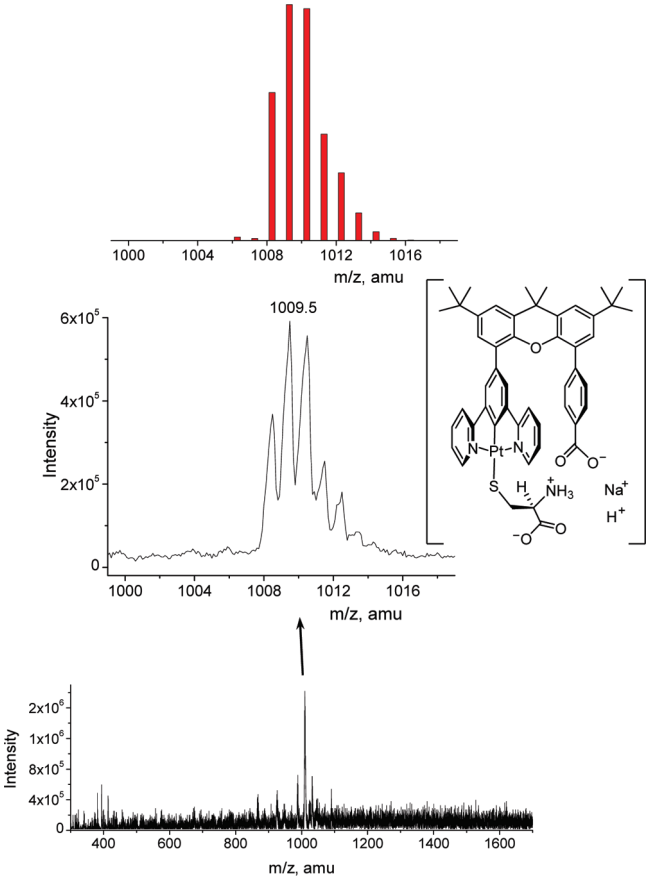


**Figure 4.** ESI mass spectra (+ve mode) of **1** ($10^{-4}$ M) and cysteine (10 equiv.) in 8:2 DMF/Tris buffer (0.005 M; NaCl, 0.05 M; pH 7.2) using zero declustering potential: (bottom) full spectrum; (middle) $[\mathbf{1} - \mathrm{Cl} + \mathrm{Cys} + \mathrm{Na}]^+$ species at $m/z$ = 1009.5; (top) calculated isotopic distribution.

performed to study the response of **1** to Cys and the homologous relative homocysteine (Hcy), while the medium was changed to aerated 8:2 DMF/Tris buffer (pH 7.2)[14] to enable comparisons with the nonionizable complex **2**. The UV−vis spectral changes for **1** with Cys feature a bathochromic shift for the lowest-energy MLCT absorption and reveal a well-defined isosbestic point at 424 nm, which was subsequently used as the emission $\lambda_{ex}$ (Figure 5). The observed red shift for the MLCT absorption band of **1** upon treatment with Cys may be tentatively ascribed to the nature of the resultant Pt−S(Cys) species and the electron-rich thiolate donor, which would reduce the electrophilicity of the Pt center and stabilize the MLCT transition.

In the emission titrations, incremental quenching is detected upon gradual addition of Cys. Concomitantly, the aerated emission lifetime ($\tau_{504}$ = 0.4 $\mu$s) remains constant, which indicates static quenching and presumably rules out other plausible quenching pathways such as intermolecular electron transfer. To rationalize the observed quenching, we suggest that the presumed substitution of chloride for the thiolate fragment would confer increased flexibility and

(22) The observed emission quenching and red-shifted MLCT absorption are also consistent with the introduction of greater ligand-to-ligand charge transfer (LLCT) character. Similar changes have been detected for related Pt(II) systems upon incorporation of electron-rich substituents: (a) Wong, K. M. C.; Tang, W. S.; Lu, X. X.; Zhu, N.; Yam, V. W. W. *Inorg. Chem.* **2005**, *44*, 1492. (b) Han, X.; Wu, L.-Z.; Si, G.; Pan, J.; Yang, Q.-Z.; Zhang, L.-P.; Tung, C.-H. *Chem.—Eur. J.* **2007**, *13*, 1231.

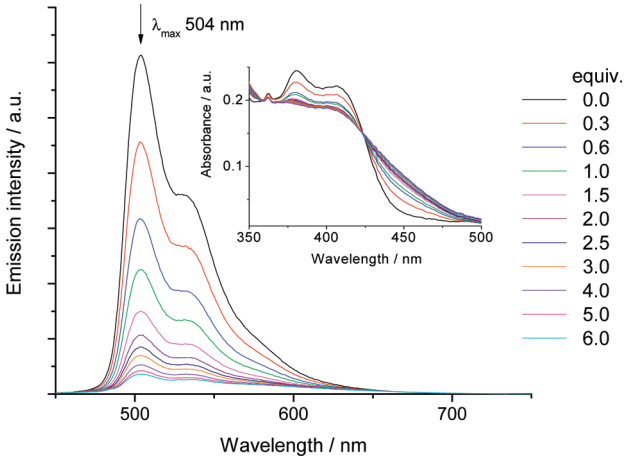


**Figure 5.** Quantitative emission ($\lambda_{ex}$ 424 nm) and UV−vis (inset) titrations for **1** ($5.0 \times 10^{-5}$ M) upon addition of cysteine (stock: $2.0 \times 10^{-2}$ M) in aerated 8:2 DMF/Tris buffer (pH 7.2).

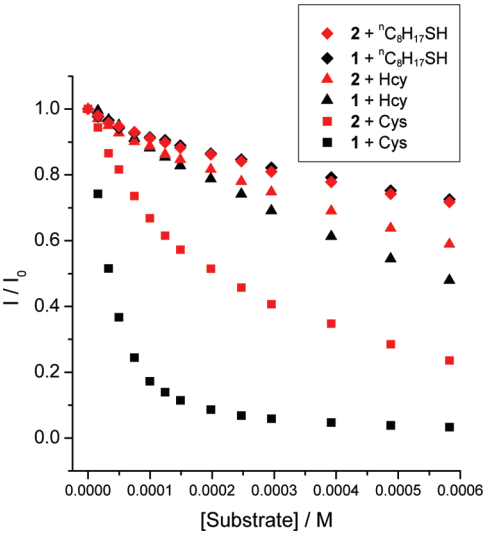


**Figure 6.** Binding isotherms for **1** (black) and **2** (red) ($5.0 \times 10^{-5}$ M) with thiol substrates in aerated 8:2 DMF/Tris buffer (pH 7.2).

facilitate nonradiative decay pathways, while the attachment of additional polar/charged moieties to the luminophore can enhance solvent quenching processes.[22] Optimal curve fitting for 1:1 binding was performed for the emission spectral changes, and the log $K$ was determined to be 4.90 ± 0.01 (Supporting Information). Emission titrations for **2**, and with Hcy and the nonbiological 1-octanethiol, were also performed to gain insight into the binding interaction and mechanism, and the revealing results are summarized in Figure 6 and Table 2.

First, the almost identical binding isotherms and log $K$ values for **1** and **2** with 1-octanethiol are strongly suggestive of negligible involvement by the carboxylate/ester moiety and a simple substitution of $Cl^-$ by the $^nC_8H_{17}S^-$ nucleophile. Second, both **1** and **2** bind more strongly to Hcy than 1-octanethiol. The slightly higher log $K$ for **1** (Supporting Information) may indicate that, although the ester unit in **2** can engage in ion-dipole H-bonding (MeOC═O···$H^+$−N) with Hcy, the corresponding Coulombic attraction between **1** and Hcy ($CO_2^-$···$H^+$−N) should be more favorable. Third, the binding to Cys is clearly the strongest for both **1**

**Table 2. Calculated log *K* for 1 and 2 with Thiol Substrates (1:1 binding) in Aerated 8:2 DMF/Tris Buffer (pH 7.2)**

| thiol substrate | 1 | 2 |
|---|---|---|
| cysteine | log $K = 4.90 \pm 0.01$ | log $K = 3.80 \pm 0.07$ |
| homocysteine | log $K = 3.65 \pm 0.06$ | log $K = 3.42 \pm 0.11$ |
| 1-octanethiol | log $K = 2.93 \pm 0.03$ | log $K = 2.94 \pm 0.03$ |

and **2**, and the above Coulombic argument is again invoked to rationalize the significantly higher log *K* for **1**, as predicted by the DFT calculations described above.

Previously reported luminescent and colorimetric probes for biological thiols are often nondiscriminating,[23,24] or selectivity for Hcy over Cys is obtained (due to steric reasons).[25] Indeed, sensors capable of Cys-over-Hcy selectivity are rare.[26] In this context, the noticeably higher log *K* for the binding of **1** to Cys compared with Hcy is intriguing. Even though the selectivity for Cys over Hcy ($K_{Cys}/K_{Hcy} = 17.8$) is modest, we suggest that the binding cavity in **1** affords a superior ditopic spatial fit and enhanced complementarity for the shorter Cys. Hence, we consider the preferential binding of **1** to the more sterically hindered Cys over Hcy to be the initial realization of the crowded ditopic phosphorescent host concept postulated in this work. The selective recognition of biomolecules and their structural motifs is appealing for, inter alia, probing biological pathways and designing new therapeutic agents. The detection of Cys and Hcy is important because abnormal levels of these biological thiols are associated with a wide spectrum of human diseases such as neurotoxicity, growth problems, and cardiovascular and Alzheimer's diseases.[27]

## Summary

Compared with our recent report employing terpyridine-Pt(II) moieties, the present work describes a host system containing the highly emissive [N,C,N-Pt(II)] luminophore. The new complexes have been fully characterized, and their photophysical properties and potential to act as selective phosphorescent probes have been investigated. By utilizing the known propensity for terminal thiols to coordinate to Pt(II), we have integrated the [N,C,N-Pt(II)] and carboxylate binding sites to afford a crowded molecular framework that displays unusual preferential binding for Cys over Hcy, while no binding is detected for methionine. In this regard, the preorganized, shape-persistent binding pocket maintained by the rigid xanthene backbone undoubtedly plays a critical role in differentiating the thiol-containing species, and the enhanced binding with Cys is attributed to the superior ditopic spatial fit and greater complementarity. Insight into the nature of the host−guest interaction has also been obtained from the binding behavior of the ester congener. While we are not advocating this system as a practical sensor for distinguishing biological thiols (the sensing media are not biocompatible), we consider that the development of this design approach, based on congested ditopic hosts bearing responsive phosphorescent reporting units, is worthwhile.

## Experimental Section

**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. $^1$H NMR spectra were obtained on a Bruker DRX 400 FT-NMR spectrometer (ppm) using $Me_4Si$ as internal standard. ESI mass spectra were measured on a Perkin-Elmer Sciex API 150EX 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.

**Photophysical Measurements.** 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. Low-temperature (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. Unless otherwise stated, 298 K emission spectra were recorded using aerated solutions. The emission quantum yield was measured[28] by using $[Ru(bpy)_3](PF_6)_2$ 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 $\Phi$ is the luminescence quantum yield; sample and standard solutions for this purpose were degassed with at least three freeze−pump−thaw cycles. 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 $\lambda$ (±1 nm), $\tau$ (±10%), and $\Phi$ (±10%) are estimated. For the UV−vis absorption and emission

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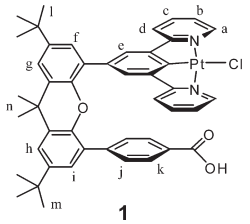
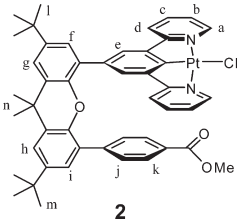
titration experiments, the platinum complexes (50 $\mu$M) in $CH_3CN$/Tris (1:1 v/v; 5% DMF) or DMF/Tris (8:2 v/v) solution were titrated with amino acids and other thiol-containing substrates (20 mM) dissolved in Tris buffer. The emission and UV−vis absorption spectra of the aerated solution were measured after successive additions of the substrate solution at 1 min intervals.

**Synthetic Procedures.** Synthetic details for the ligands are given in the Supporting Information. Complex **1**: A mixture of $K_2PtCl_4$ (0.062 g, 0.148 mmol) in water (3 mL) and the N,C,N-xanthene-benzoic acid ligand (0.100 g, 0.148 mmol) in $CH_3CN$/$CH_2Cl_2$ (10 mL, 9:1) was refluxed for 72 h to give a yellow solution. The organic phase was extracted with $CH_2Cl_2$ (50 mL) and washed with water (3 × 50 mL). The solvent was then removed by evaporation in vacuo, and the resultant residue was washed with pentane, then recrystallized by vapor diffusion of $Et_2O$ into a $CH_2Cl_2$ mixture to give a yellow solid (0.088 g, 66%). Anal. Calcd for $C_{46}H_{43}ClN_2O_3Pt$ (902.38): C, 61.23; H, 4.80; N, 3.10. Found: C, 61.54; H, 5.19; N, 3.06. IR (KBr, $cm^{-1}$): 3450, 2960, 1720. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 9.22−9.21 (m, 2H, $H_a$), 7.93−7.89 (m, 2H, $H_c$), 7.52−7.51 (m, 2H, $H_{g,h}$), 7.42 (d, $J$ = 8.3 Hz, 4H, $H_{d,k}$), 7.38 (s, 2H, $H_e$), 7.36−7.34 (m, 2H, $H_b$), 7.32 (d, $J$ = 2.3 Hz, 1H, $H_{f/i}$), 7.27 (d, $J$ = 8.3 Hz, 2H, $H_j$), 7.21 (d, $J$ = 2.3 Hz, 1H, $H_{f/i}$), 2.96 (s, 1H, OH; assigned using $D_2O$), 1.78 (s, 6H, $H_n$), 1.40 (s, 9H, $H_{l/m}$), 1.36 (s, 9H, $H_{l/m}$). $^{13}$C NMR (101 MHz, $CD_2Cl_2$): $\delta$ 167.5, 167.5, 167.4, 160.0, 152.3, 146.3, 146.2, 145.5, 145.1, 143.1, 140.9, 139.5, 133.75, 130.3, 130.3, 129.9, 129.7, 128.5, 128.1, 126.2, 126.1, 125.9, 123.9, 123.3, 122.7, 119.8, 35.4, 34.9, 34.9, 32.9, 31.7, 31.7. ESI-MS (+ve mode, MeOH): $m/z$ 903 $[M + 1]^+$.




**1**

Complex **2** was similarly prepared using the N,C,N-xanthene-ester ligand. The solvent was evaporated in vacuo, and purification by column chromatography on alumina oxide (gradient elution from 100% hexane to 8:2 $CH_2Cl_2$/MeOH) afforded a yellow solid (0.061 g, 51%). Recrystallization in a $Et_2O$/MeOH mixture gave small yellow crystals. Anal. Calcd for $C_{47}H_{45}ClN_2O_3Pt$ (916.40): C, 61.60; H, 4.95; N, 3.06. Found: C, 61.37; H, 5.23; N, 3.17. IR (KBr, $cm^{-1}$): 2960, 1700. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 9.29−9.28 (m, 2H, $H_a$), 7.89 (t, $J$ = 7.8 Hz, 2H, $H_c$), 7.52−7.51 (m, 2H, $H_{g,h}$), 7. 42 (d, $J$ = 7.9 Hz, 2H, $H_d$), 7.41 (s, 2H, $H_e$), 7.41 (d, $J$ = 7.9 Hz, 2H, $H_k$), 7.33−7.31 (m, 3H, $H_{b, f/i}$), 7.28 (d, $J$ = 7.7 Hz, 2H, $H_j$), 7.20 (d, $J$ = 2.2 Hz, 1H, $H_{f/i}$), 3.87 (s, 3H, OMe), 1.77 (s, 6H, $H_n$), 1.40 (s, 9H, $H_{l/m}$), 1.35 (s, 9H, $H_{l/m}$). $^{13}$C NMR (101 MHz, $CD_2Cl_2$): $\delta$ 167.7, 166.4, 160.9, 152.2, 146.3, 146.2, 145.6, 145.1, 142.9, 141.0, 139.4, 133.5, 130.3, 130.3, 130.0, 129.7, 129.2, 128.4, 128.3, 126.4, 126.3, 126.0, 123.6, 123.3, 122.6, 119.8, 52.5, 35.4, 34.9, 34.9, 32.9, 31.7, 31.6. ESI-MS (+ve mode, MeOH): $m/z$ 917 $[M + 1]^+$.




**2**

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**Supporting Information Available:** CIF for **2**; experimental details and characterization data; photophysical data and spectra; curve fittings for substrate binding; details of molecular modeling. This material is available free of charge via the Internet at http://pubs.acs.org.