

Microarray pattern recognition based on Pt^{II} terpyridyl chloride complexes: vapochromic and vapoluminescent response†

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Received (in Cambridge, UK) 23rd July 2008, Accepted 2nd October 2008

First published as an Advance Article on the web 21st October 2008

DOI: 10.1039/b812634h

Eighteen distinct Pt^{II} terpyridyl chloride cross-reactive sensor elements incorporated into microarrays with 1000 × 250 μm well dimensions generate distinctive colorimetric and luminometric responses upon exposure to a variety of volatile organic compounds (VOCs).

The development of sensory systems displaying rapid real-time response to chemical and biological analytes continues to lie at the forefront of fundamental research. Significant focus has been placed on the development of chemo-sensors containing receptors that selectively bind and respond to the species of interest. This methodology requires significant synthetic effort and the sensing entity is generally designed for specificity, thereby limiting potentially valuable cross-reactivity towards a broader range of analytes. More recently, efforts have been oriented towards the design of molecules displaying indiscriminant non-selective responses. In some instances, these molecules have been incorporated into arrays, producing colorimetric patterns that are unique to each combination of sensor and analyte.^{1–9}

Square planar Pt^{II} salts are particularly amenable towards pattern recognition-based chemical sensing as their spectroscopic and photophysical properties in the solid state are readily tuned by vapor sorption. For example, Pt^{II} double salts display dramatic color changes towards exposure to different VOCs resulting from non-covalent analyte interactions (including hydrogen bonding and lipophilic interactions) and modification of the lattice (expansion or contraction) modulating the distance between metal centers.^{10–15} More recently, numerous examples of vapochromic Pt^{II} polypyridyl complexes have emerged.^{14–22} These structures benefit from favorable π–π stacking between ligands in adjacent structures which assist in promoting metal–metal σ-interactions.^{19,20}

This combination of effects produce absorption and emission colors in the solid state spanning the visible spectrum, coarsely tuned with variation in the counterion. The vapochromic properties of specific individual Pt^{II} polypyridyl complexes in the solid state have been detailed by several groups.^{16–24}

The present work focuses on the preparation of microarrays containing 18 distinct cross-reactive Pt^{II} terpyridyl chloride complexes possessing relevant variation in ligand structure

and counterion, Fig. 1. Most of the complexes are new and their syntheses, based on established procedures,^{25–29} and structural characterization are provided as ESI.† The alkoxy-modified terpyridyl ligands were chosen as they are documented to favor π-stacking,²⁴ thereby enabling the possibility of enhanced metal–metal interactions in the solid state. The Pt^{II} complexes bearing 4,4',4''-*t*-Bu₃-2,2':6',2''-terpyridine and 2,2':6',2''-terpyridine were included to glean further insight regarding ligand substituent influence on the vapochromic and vapoluminescent response of these molecules to different VOCs. Variation in counterion size perturbs the lattice, producing different solid state vapochromic response characteristics from otherwise identical molecular compounds.

The color of each individual Pt^{II} solid varies from yellow to red and most of them show immediate colorimetric changes upon exposure to different chemical vapors. However, the main goal of the present study is to incorporate all 18 cross-reactive complexes into microarrays to qualitatively mimic the olfactory system, producing distinct colorimetric/luminometric patterns upon exposure to different VOCs.^{7,30} The microarrays reported here are intended to illustrate qualitative vapochromic and vapoluminescent responses, precise quantification of the relevant changes are the subject of a lengthy study currently in progress.

Solutions of each metal complex were prepared in DMSO (conc. 2.0 × 10^{−2} M) and injected into the multi-well microplates using a microsyringe, producing the final sensor arrays displayed in Fig. 2 and 3; each well contains 4 nmol of Pt^{II} metal complex. The microplates were produced by ultrasonic drilling of microscope slides as previously described (Fig. 4).^{3,4,31} The images of the microplates were obtained using a flatbed scanner measuring the colorimetric and

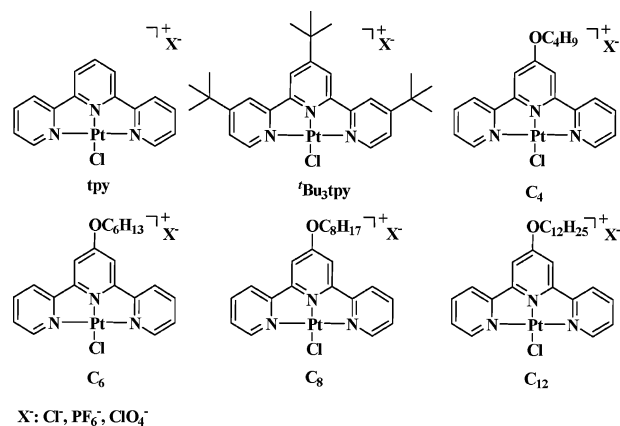


Fig. 1 Chemical structures of the Pt^{II} terpyridyl chloride salts used as cross-reactive microarray sensors.

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† Electronic supplementary information (ESI) available: Synthetic details, complete characterization of ligands and complexes, and data on recycling the sensor arrays. See DOI: 10.1039/b812634h

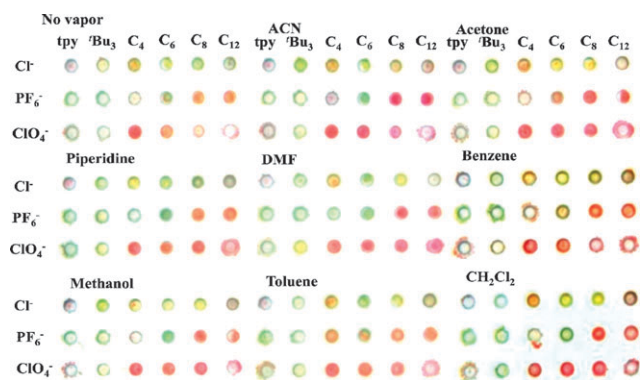


Fig. 2 Vapochromic colorimetric response of the Pt^{II} terpyridyl chloride-based microarrays towards different VOCs.

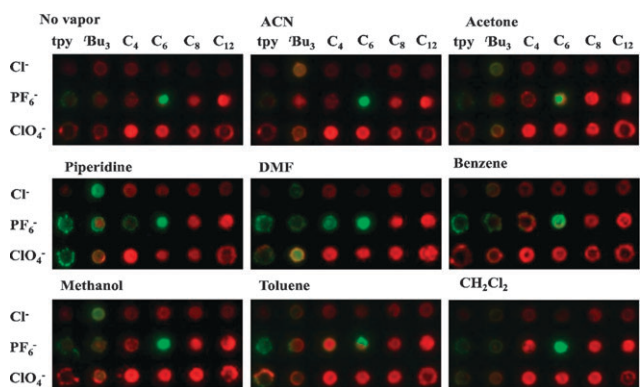


Fig. 3 Vapoluminescent response of the Pt^{II} terpyridyl chloride-based microarrays towards different VOCs. The arrays were excited using a broadband UV lamp (300–400 nm, $\lambda_{\text{max}} = 365 \text{ nm}$).³⁰

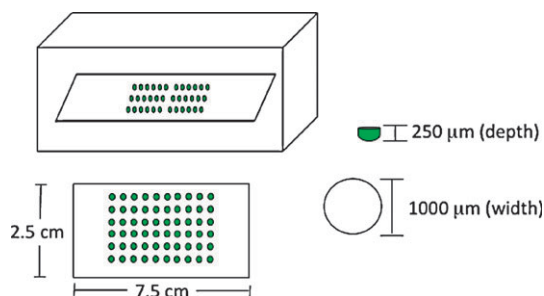


Fig. 4 Schematic representation of the microplates and the chamber used in the present microarray-based vapochromic study.

luminometric changes in the red, green, and blue (RGB) channels. For data analysis, the images in the three channels were merged using an imaging program to obtain the final RGB pictures. Even though in most instances an immediate response was observed, the microplates were exposed to individual vapors in a rubber-sealed chamber (Fig. 4) for 120 min to ensure that equilibrium was established. The images were taken before and after vapor exposure. Comparison of the arrays upon exposure to different vapors permits visualization of qualitative pattern changes in the response. Although the vapor sorption process is reversible, each time a new analyte was tested, a freshly prepared array was utilized.

Some of the complexes displayed color changes that are readily discriminated by the naked eye, Fig. 2. Examples

include the PF₆[−] salts of the Pt^{II} complexes bearing C₄, C₈, and C₁₂ alkoxy chains in addition to the ClO₄[−] salts of complexes C₄–C₁₂. In all cases, the complexes turned deep red in the presence of ACN within a matter of seconds. The same complexes are also responsive towards acetone vapor, changing their color to orange while the analogous Cl[−] salts appear more yellow. For CH₂Cl₂, the C₄–C₈ complexes containing Cl[−] as counterion displayed a deepening of their yellow color, whereas the C₁₂ analog darkened. Again, the PF₆[−] salts of C₈ and C₁₂ transform to deep red in the presence of CH₂Cl₂ in addition to their ClO₄[−] counterparts (C₄–C₁₂). The other vapors tested exhibit more subtle responses requiring more detailed quantitative study beyond the scope of the current presentation. The tpy and 'Bu₃ analogs respond with very slight color modification after exposure to each vapor studied. Most notably, the 'Bu₃ ClO₄[−] complex develops an impressive change to yellow in the presence of DMF, however, the remaining responses appear to be faint at best, and will require more detailed analysis. A representative analysis for acetone is provided as ESI.†

From the luminometric point of view, in absence of vapors, the chloride salts in general are the least emissive of the series. Notably, all six Pt^{II} complexes bearing the BPh₄[−] counterion (data not shown) are non-emissive in the solid state and no discernable changes were observed upon exposure to any of the vapors utilized in this study. The Pt^{II} complexes containing tpy or 'Bu₃tpy as ligands displayed mild “turn-on” responses to piperidine, methanol, ACN, DMF, toluene, acetone, and benzene, Fig. 3. The strongest emission enhancements were observed in the array exposed to ACN. Exposure to acetone enabled a “turn-on” emission response in all the elements of the array including the chloride salts with the exception of the tpy analogs which appear to be non-responsive by the naked eye. In many instances, the arrays exhibit a hypsochromic emission shift when exposed to benzene, piperidine, toluene, and DMF, producing bright green or yellow photoluminescence, suggesting an attenuation of metal–metal σ -interactions (lengthening of average metal–metal distance). In the case of CH₂Cl₂, luminescence changes cannot be appreciated by the naked eye in most array elements although the PF₆[−] and ClO₄[−] display slight emission enhancement. In general, most of the present molecules are quite responsive towards Lewis basic solvents in addition to volatile aromatic systems. Significant reversibility of vapor sorption was observed and the arrays can be recycled after drying in a vacuum oven. For example, the sensing of acetone was performed in one array that was recycled 5 times without any noticeable signs of degradation, Fig. S2–S4, ESI†. Interestingly, acetonitrile was found to be the most difficult analyte in the series to remove from the sensor microarrays suggesting that this Lewis base strongly associates with the coordinatively unsaturated Pt^{II} complexes.

We have demonstrated that is indeed possible to assemble vapochromic and vapoluminescent microarrays for pattern recognition using 18 structurally related cross-reactive Pt^{II} terpyridyl chloride complexes. The current molecules are synthetically facile and their rapid and qualitative colorimetric/luminometric changes towards VOC's are tuned with variation in both counterion and ligand structure, making it

possible to construct microarrays of complexes that respond distinctively to different analytes. The VOCs that induce the greatest vapochromic and vapoluminescent changes are those containing lone pairs such as acetonitrile, piperidine, and DMF. Volatile aromatics also induce unique colorimetric and luminometric response in several instances, potentially relevant for the detection of nitroaromatics.

This research was supported by the Air Force Office of Scientific Research (FA9550-05-1-0276), the National Science Foundation (CBET-0731153 and CHE-0719050) and the ACS-PRF (44138-AC3). M.L.M. acknowledges support from a McMaster Fellowship. Special thanks is given to the Prof. P. Anzenbacher Jr. research group at BGSU, particularly M. A. Palacios, for providing technical assistance in the measurement and analysis of the microarray responses reported.

Notes and references

- 1 T. Hirsch, H. Kettenberger, O. S. Wolfbeis and V. M. Mirsky, *Chem. Commun.*, 2003, 432–433.
- 2 J. J. Lavigne and E. V. Anslyn, *Angew. Chem., Int. Ed.*, 2001, **40**, 3118–3130.
- 3 M. A. Palacios, R. Nishiyabu, M. Marquez and P. Anzenbacher, Jr, *J. Am. Chem. Soc.*, 2007, **129**, 7538–7544.
- 4 M. A. Palacios, Z. Wang, V. A. Montes, G. V. Zyryanov, B. J. Hausch, K. Jursikova and P. Anzenbacher, Jr, *Chem. Commun.*, 2007, 3708–3710.
- 5 S. L. Wiskur, P. N. Floriano, E. V. Anslyn and J. T. A. McDevitt, *Angew. Chem., Int. Ed.*, 2003, **42**, 2070–2072.
- 6 A. T. Wright and E. V. Anslyn, *Chem. Soc. Rev.*, 2006, **35**, 14–28.
- 7 C. Zhang and K. S. Suslick, *J. Am. Chem. Soc.*, 2005, **127**, 11548–11549.
- 8 T. A. Dickinson, J. White, J. S. Kauer and D. R. Walt, *Nature*, 1996, **382**, 697–700.
- 9 K. J. Albert, N. S. Lewis, C. L. Schauer, G. A. Sotzing, S. E. Stitzel, T. P. Vaid and D. R. Walt, *Chem. Rev.*, 2000, **100**, 2595–2626.
- 10 C. E. Buss, C. E. Anderson, M. K. Pomije, C. M. Lutz, D. Britton and K. R. Mann, *J. Am. Chem. Soc.*, 1998, **120**, 7783–7790.
- 11 C. E. Buss and K. R. Mann, *J. Am. Chem. Soc.*, 2002, **124**, 1031–1039.
- 12 C. A. Daws, C. L. Exstrom, J. R. Sowa, Jr and K. R. Mann, *Chem. Mater.*, 1997, **9**, 363–368.
- 13 S. M. Drew, D. E. Janzen, C. E. Buss, D. I. MacEwan, K. M. Dublin and K. R. Mann, *J. Am. Chem. Soc.*, 2001, **123**, 8414–8415.
- 14 C. L. Exstrom, M. K. Pomije and K. R. Mann, *Chem. Mater.*, 1998, **10**, 942–945.
- 15 C. L. Exstrom, J. R. J. Sowa, C. A. Daws, D. Janzen, K. R. Mann, G. A. Moore and F. F. Stewart, *Chem. Mater.*, 1995, **7**, 15–17.
- 16 S. M. Drew, D. E. Janzen and K. R. Mann, *Anal. Chem.*, 2002, **74**, 2547–2555.
- 17 P. Du, J. Schneider, W. W. Brennessel and R. Eisenberg, *Inorg. Chem.*, 2008, **47**, 69–77.
- 18 L. J. Grove, J. M. Rennekamp, H. Jude and W. B. Connick, *J. Am. Chem. Soc.*, 2004, **126**, 1594–1595.
- 19 W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, Z. He and K.-Y. Wong, *Chem.–Eur. J.*, 2003, **9**, 6155–6166.
- 20 T. J. Wadas, Q.-M. Wang, Y.-j. Kim, C. Flaschenreim, T. N. Blanton and R. Eisenberg, *J. Am. Chem. Soc.*, 2004, **126**, 16841–16849.
- 21 V. W.-W. Yam, K. H. Y. Chan, K. M.-C. Wong and N. Zhu, *Chem.–Eur. J.*, 2005, **11**, 4535–4543.
- 22 V. W.-W. Yam, K. M.-C. Wong and N. Zhu, *J. Am. Chem. Soc.*, 2002, **124**, 6506–6507.
- 23 L. J. Grove, A. G. Oliver, J. A. Krause and W. B. Connick, *Inorg. Chem.*, 2008, **47**, 1408–1410.
- 24 J. S. Field, R. J. Haines, D. R. McMillin and G. C. Summerton, *J. Chem. Soc., Dalton Trans.*, 2002, 1369–1376.
- 25 P. R. Andres, R. Lunkwitz, G. R. Pabst, K. Böhn, D. Wouters, S. Schmatloch and U. S. Schubert, *Eur. J. Org. Chem.*, 2003, 3769–3776.
- 26 M. Heller and U. S. Schubert, *Eur. J. Org. Chem.*, 2003, 947–961.
- 27 S.-W. Lai, M. C. W. Chan, K.-K. Cheung and C.-M. Che, *Inorg. Chem.*, 1999, **38**, 4262–4267.
- 28 V. Kukushkin, A. Pombeiro, C. Ferreira and L. Elding, *Inorg. Synth.*, 2002, **33**, 189–195.
- 29 H. K. Yip, L. K. Cheng, K.-K. Cheung and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1993, 2933–2938.
- 30 N. A. Rakow and K. S. Suslick, *Nature*, 2000, **406**, 710–713.
- 31 R. Nishiyabu, M. A. Palacios, W. Dehaen and P. Anzenbacher, Jr, *J. Am. Chem. Soc.*, 2006, **128**, 11496–11504.