COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Self-aggregated phosphorescent platinum(II) polymeric material from modified poly(4-vinylpyridine)†

Chi-Chung Kwok, Sze-Chit Yu, Iona H. T. Sham and Chi-Ming Che*

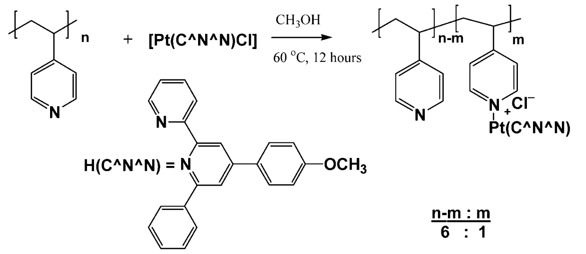
Department of Chemistry and the HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, China. E-mail: cmche@hku.hk; Fax: 852-28571586

Received (in Cambridge, UK) 21st June 2004, Accepted 18th August 2004
First published as an Advance Article on the web 27th September 2004

A solvochromic material made from incorporation of photoluminescent Pt(II)(C^N^N) moieties into commercially available homopolymer poly(4-vinylpyridine) exhibits different emission energies, due to different degrees of self-aggregation in various solvents and as thin film upon exposure to vapour of different volatile organic compounds (VOC); self-aggregation enables intra- and intermolecular interactions arising from π-stacking of the Pt(C^N^N) moieties, which is affected by medium polarity.

Self-aggregated polymers have gained a lot of attention recently, due to their interesting morphological behaviour and well-defined nanostructures. These systems are studied not only for basic research interest,[1,2] but also for a variety of potential applications such as bioreactors,[3] drug and gene delivery,[4,5] separation[6] and sensing technology,[7] as well as surface modifications.[8] Most self-aggregated polymeric systems are based on block and graft copolymers.[9–11] Some of these block copolymers contain polar and non-polar segments. Due to different solubility of the blocks in a specific solvent, various types of aggregates such as spherical, rod-like or disk-like structures can be formed.[12] In this work, a self-aggregated polymer made from homopolymer poly(4-vinylpyridine) (PVP) and cyclometalated Pt(II)(C^N^N) (HC^N^N = 4-(4-methoxyphenyl)-6-phenyl-2,2′-bipyridine) complex has been developed (Scheme 1). Such a system, abbreviated as PVP–Pt(C^N^N), can be easily prepared through reacting commercially available PVP with [Pt(C^N^N)Cl] in CH_3OH at 60 °C for 12 hours. Thermogravimetric analysis showed that the product (Pt content = 14.5% by weight, as determined by ICP-MS; $n - m : m = 6 : 1$, Scheme 1) is stable up to 302 °C.

PVP–Pt(C^N^N) possesses intriguing solvochromic emission properties. The polymeric material exhibits photoluminescence (PL) with λ_{max} at 550 nm in DMF (*N,N′*-dimethylformamide) and 558 nm in CH_2Cl_2; the emission is attributed to the triplet metal-to-ligand charge transfer (^{3}MLCT) excited state of the Pt(C^N^N) moiety.[13] In $CHCl_3$ or CH_3OH solution, the emission λ_{max} red-shifts to 637 and 645 nm respectively. Fig. 1 shows the shift in PL emission upon changing the ratio of CH_2Cl_2 to CH_3OH in the solution. The two emissions (λ_{max} at 558 and 645 nm) exist when both solvents are present, with the relative intensity of the 645 nm component increasing and that of the 558 nm component decreasing with descending ratio of CH_2Cl_2 to CH_3OH. Since the PL emission of the model compound, [Pt(C^N^N)py]Cl (py = pyridine) does not undergo such a substantial shift in λ_{max} upon changing the solvent from CH_2Cl_2 to CH_3OH, the 645 nm emission of the PVP–Pt(C^N^N) material in CH_3OH solution could not be only due to a solvation effect (λ_{max} of [Pt(C^N^N)py]Cl = 551 nm in DMF, 558 nm in CH_2Cl_2, 560 nm in $CHCl_3$ and 547 nm in CH_3OH). With reference to previous work,[14] this emission is assigned to triplet metal–metal-to-ligand charge transfer (^{3}MMLCT).



Scheme 1 Synthetic scheme of PVP–Pt(C^N^N).

To probe the self-aggregation behaviour of PVP–Pt(C^N^N), the particle size distribution of the polymer in various solvents was studied using Zetasizer based on photo-correlation spectroscopy (PCS). The extent of self-aggregation of PVP–Pt(C^N^N) can be reflected by its solubility in the solvent. In this work, PVP was found to have a good solubility in CH_2Cl_2, $CHCl_3$, CH_3OH and DMF, and its particle sizes in these solvents are about the same (19, 17, 19 and 15 nm respectively). Upon incorporation of the Pt(C^N^N) moieties, the particle diameter of PVP–Pt(C^N^N) in these solvents follows the solubility trend: DMF > CH_2Cl_2 > CH_3OH ~ $CHCl_3$, with the smallest particles found in the most soluble solvent and *vice versa* (24 nm in DMF, 27 nm in CH_2Cl_2, 49 nm in CH_3OH and 92 nm in $CHCl_3$).

Results from the above studies indicate that there could be a relationship between the solubility, thus the aggregation behaviour, of PVP–Pt(C^N^N) and the shift in emission λ_{max} in these solvents. The solvochromic effect of PVP–Pt(C^N^N) in solution that leads to a 637 or 645 nm emission in $CHCl_3$ or CH_3OH solution originates from π-stacking interactions between the Pt(C^N^N) chromophores in the ground and/or excited state.[13] Due to a different degree of solubility in the solvent, a different extent of self-aggregation of the polymer chain is brought about. With a greater extent of aggregation in the less solubilising solvents such as CH_3OH and $CHCl_3$, there could be a decrease in separation between the Pt(C^N^N) units. Consequently, intra- and intermolecular interactions between the Pt(C^N^N) moieties are introduced,

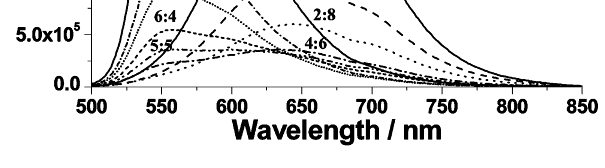


Fig. 1 Solution emission spectra for PVP–Pt(C^N^N) in various CH_2Cl_2/CH_3OH mixtures.

---

† Electronic supplementary information (ESI) available: procedures for synthesis and preparation of samples for various measurements; data illustrating the change in physical and PL behaviour of PVP–Pt(C^N^N). See http://www.rsc.org/suppdata/cc/b4/b409333j/

DOI: 10.1039/b409333j

thereby giving rise to the ^{3}MMLCT excited state. To verify this hypothesis, a PVP–Pt(C^N^N-*t*Bu) (HC^N^N-*t*Bu = 4,4′-di(*tert*-butyl)-6-phenyl-2,2′-bipyridine) derivative was prepared; Pt(C^N^N-*t*Bu) has two *t*-butyl groups at the *para* position of the two pyridine rings, and was designed to eliminate intra- and intermolecular interactions. The emission λ_{max} for the PVP–Pt(C^N^N-*t*Bu) derivative in CH_3OH is at 527 nm; no ^{3}MMLCT emission was observed.

The PL emission λ_{max} of PVP–Pt(C^N^N) thin film in air is at 573 nm, which occurs at a similar energy to the ^{3}MLCT emission of the [Pt(C^N^N)] moiety.[13] Notably, the PL emission of PVP–Pt(C^N^N) thin film is responsive to the presence of volatile organic solvent vapour. The emission λ_{max} red-shifted when the film was placed in an atmosphere saturated with the vapour of polar solvents (Group A): $CHCl_3$ (λ_{max} at 598 nm), CH_2Cl_2 (623 nm) and CH_3OH (633 nm), while little change was observed with non-polar solvents (Group B): hexane (583 nm) and benzene (572 nm). When the vapour of polar organic solvent was removed and the film was dried, the emission λ_{max} shifted back to its original position of 573 nm.

To further study the effect of medium polarity, the emission of PVP–Pt(C^N^N) in methanoic solution at different ionic strengths was examined.[15] Fig. 2 shows the relationship between the concentration of salt and the intensity of 645 nm emission of PVP–Pt(C^N^N) in methanoic solution. The emission intensity first increased, and eventually stabilised with increasing ionic strength. For a specific concentration, salts with a divalent cation such as Zn^{2+} or Ca^{2+} gave more enhancement in emission intensity than those with a monovalent cation like Na^+, K^+ or Bu_4N^+. The Bu_4N^+ and Na^+ cations were found to give similar results. These observations are in accordance with the results obtained by exposing the PVP–Pt(C^N^N) film to saturated vapour of various organic solvents, where the ^{3}MMLCT emission at 645 nm was enhanced with the vapour of polar solvents. It is known that an increase in concentration and hence ionic strength of a polyelectrolyte solution can result in a decrease in polymer coil dimensions.[16] The adsorption and/or penetration of polar solvent molecules into the PVP–Pt(C^N^N) film or increased ionic strength of the methanoic PVP–Pt(C^N^N) solution could stabilize the positively charged Pt(C^N^N) units, and cause the polymer to adopt a more compact conformation. With a compact conformation, the Pt(C^N^N) units are brought closer together and the probability of having intra- or intermolecular interactions is increased,[17] thereby leading to an enhancement of the ^{3}MMLCT emission.

The morphology of PVP–Pt(C^N^N) films obtained upon formation of micelles prepared using CH_2Cl_2, toluene and water was studied using transmission electron microscopy (TEM). Under the electron microscope, PVP–Pt(C^N^N) was observed to aggregate and form spherical structures (Fig. 3). The dimensions of the micelles ranged from 50 to 100 nm. The micelle solution was stable at ambient temperature.

The PVP–Pt(C^N^N) thin film system requires a simpler sensor configuration than the electrochemical sensors,[18] field effect transistor devices[19] or hybrid sensor arrays[20] for detection of VOC. A sensing system with a platinum(II) complex embedded in nafion and silica materials was recently reported for detection of VOC;[21] however, phase separation of the Pt- chromophore from the inorganic host presents a problem. In the case of PVP–Pt(C^N^N), the backbone PVP can be processed in solution, and good transparent thin film can be easily obtained *via* a casting or spin-coating method. The organic backbone also presents no problem of phase separation upon incorporation of the Pt-chromophore. The response time required for the emission spectral shift of the PVP–Pt(C^N^N) film upon changing the VOCs was found to be 5–8 seconds; this is a rapid process compared to those found in similar studies.[22]

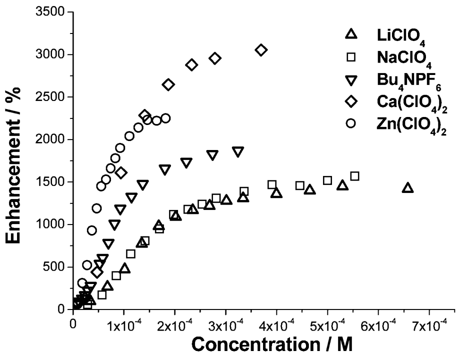


Fig. 2 Effect of concentration of salts on the 645 nm emission of PVP–Pt(C^N^N) in 0.14 g L^{-1} methanoic solution.

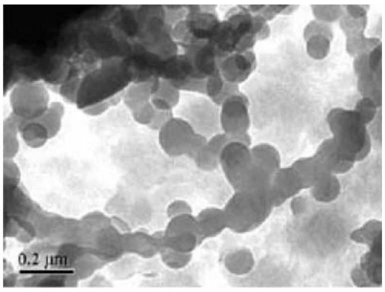


Fig. 3 Transmission electron micrograph of the micelles formed by PVP–Pt(C^N^N) in the dichloromethane–toluene–water system.

In summary, we have developed a solvochromic material made of photoluminescent platinum(II)(C^N^N) moieties incorporated into the commercially available homopolymer, poly(4-vinylpyridine). Given the diverse functional organic polymers known in the literature, such a strategy provides an entry to new classes of photoluminescent polymeric materials with potential applications in luminescent signaling.

We gratefully acknowledge financial support by the University of Hong Kong and the Innovation and Technology Commission of the Government of Hong Kong SAR, China (Project No. ITS/53/01).

Notes and references

1 L. Zhang and A. Eisenberg, *Macromolecules*, 1999, **32**, 2239.
2 A. Harada and K. Kataoka, *Macromolecules*, 2003, **36**, 4995.
3 A. Harada and K. Kataoka, *Macromolecules*, 1998, **31**, 288.
4 K. Kataoka, A. Harada and Y. Nagasaki, *Adv. Drug Delivery Rev.*, 2001, **47**, 113.
5 S. M. Mills and S. S. Davis, *Polymers in Controlled Drug Delivery*, ed. L. Illum and S. S. Davis, IOP Publishing, Bristol, 1987.
6 S. A. Jenekhe and X. L. Chen, *Science*, 1999, **283**, 372.
7 R. Chakrabarti and A. M. Kibanov, *J. Am. Chem. Soc.*, 2003, **125**, 12531.
8 S. E. Webber, *J. Phys. Chem. B*, 1998, **102**, 2618.
9 J.-F. Gohy, H. Hofmeier, A. Alexeev and U. S. Schubert, *Macromol. Chem. Phys.*, 2003, **204**, 1524.
10 H. Peng, D. Chen and M. Jiang, *J. Phys. Chem. B*, 2003, **107**, 12461.
11 K. Kataoka, H. Togawa, A. Harada, K. Yasugi, T. Matsumoto and S. Katayose, *Macromolecules*, 1996, **29**, 8556.
12 S. Hou, K. Y. K. Man and W. K. Chan, *Langmuir*, 2003, **19**, 2485.
13 S.-W. Lai, M. C.-W. Chan, T.-C. Cheung, S.-M. Peng and C.-M. Che, *Inorg. Chem.*, 1999, **38**, 4046.
14 W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, C. Li and Z. Hui, *J. Am. Chem. Soc.*, 2004, **126**, 7639.
15 D. Skoog, D. M. West and F. J. Holler, *Fundamentals of Analytical Chemistry*, Thomson Learning, New York, 1988.
16 J. E. Guillet, *Polymer Photophysics and Photochemistry*, Cambridge University Press, New York, 1985.
17 D. M. Gravett and J. E. Guillet, *Macromolecules*, 1996, **29**, 617.
18 P. M. Vadgama and I. M. Christie, GB Patent 2315864A, 1998.
19 L. Torsi, M. C. Tanese, N. Cioffi, M. C. Gallazzi, L. Sabbatini, P. G. Zambonin, G. Raos, S. W. Meille and M. M. Giangregorio, *J. Phys. Chem. B*, 2003, **107**, 7589.
20 H. Ulmer, J. Mitrovics, G. Noetzel, U. Weimar and W. Goepel, *Sens. Actuators, B*, 1997, **43**, 24.
21 C.-M. Che, W.-F. Fu, S. W. Lai, Y.-J. Hou and Y.-L. Liu, *Chem. Commun.*, 2003, 118.
22 W. Lu, M. C. W. Chan, N. Zhu, C. M. Che, Z. He and K. Y. Wong, *Chem. Eur. J.*, 2003, **9**, 1.