

# Luminescent polymeric hybrids formed by platinum(II) complexes and block copolymers

Nijuan Liu, Baoyan Wang, Weisheng Liu and Weifeng Bu\*

Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou City, Gansu Province, China, Fax: +86 931 8912582; Tel: +86 931 8915151; E-mail: buwf@lzu.edu.cn

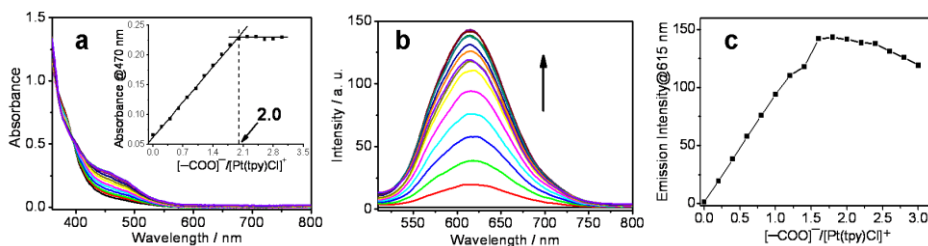
## Materials and Instruments.

Both  $[\text{Pt}(\text{Me}_2\text{bzimpy})\text{Cl}]^+\text{Cl}^-$  ( $\text{Me}_2\text{bzimpy}$  = 2,6-bis(*N*-methylbenzimidazol-2-yl)pyridine) and  $[\text{Pt}(\text{tpy})\text{Cl}]^+\text{Cl}^-$  ( $\text{tpy}$  = 2,2':6,2'-terpyridine) were prepared according to the refs 1 and 2, respectively. Both poly(ethylene oxide-*b*-acrylate sodium) ( $\text{E}_{250}\text{-}b\text{-}A_{51}$ ) and poly(styrene-*b*-acrylate sodium) ( $\text{S}_{586}\text{-}b\text{-}A_{55}$ ) were obtained from Polymer Source Inc. and used without further purification.. The numbers in subscript denote the degree of polymerization.

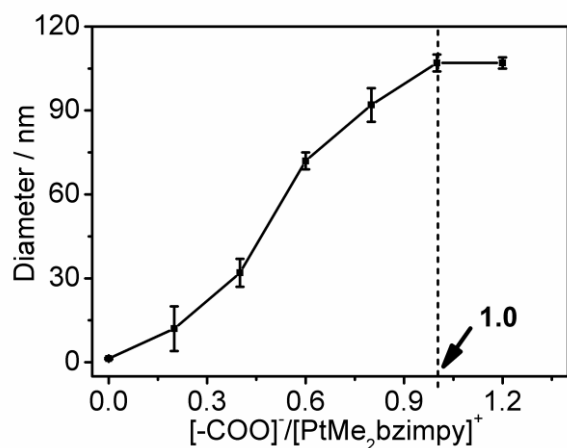
IR spectra (KBr) were measured with a Nicolet NEXUS 670 spectrometer. Dynamic light scattering (DLS) measurements were performed on a Brookhaven BI-200SM spectrometer. Bright-field TEM images were obtained with a JEOL JEM-1230 operating at 120 kV. And HAADF-STEM images and EDX measurements were performed with a FEI Tecnai F30 operating at 300 kV. Elemental analyses were performed with an Elementar VarioELcube. UV-vis Absorption spectra were recorded by using a Varian Cary 100 spectrophotometer. And luminescence measurements were made on a Hitachi F-4500 spectrofluorimeter with a xenon lamp as the excitation source. All measurements were carried out at room temperature.

## Preparation and characterization of SAP hybrids.

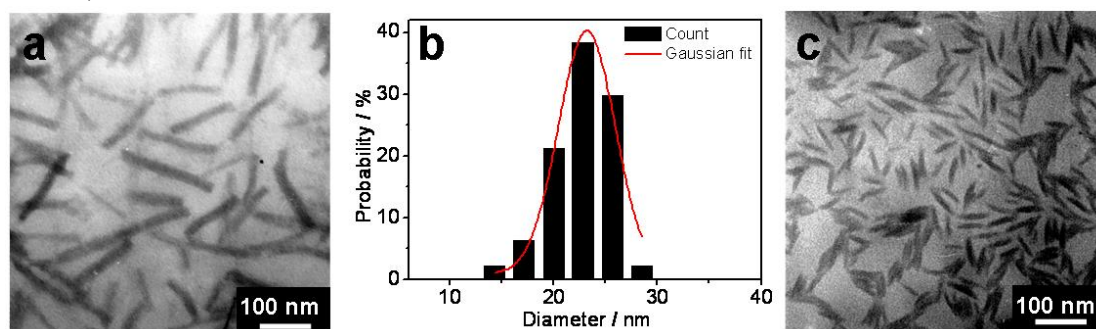
SAP-1 was prepared as follows:  $[\text{Pt}(\text{Me}_2\text{bzimpy})\text{Cl}]^+\text{Cl}^-$  (96.6 mg, 0.33 mmol) was dissolved into 20 mL of water. This solution was added to a suspension of  $\text{S}_{586}\text{-}b\text{-}A_{55}$  (52.7 mg, 0.044 mmol, based on the repeated unit of acrylate sodium) in 10 mL water with vigorous stirring. The resultant suspension was stirred for three days. The red solid was collected by filtration, washed with water, and dried in vacuum. IR (KBr): 3082, 3059, 3025, 3001, 2921, 2849, 1944, 1871, 1799, 1720, 1654, 1638, 1622, 1600, 1581, 1562, 1542, 1493, 1452, 1399, 1382, 1342, 1251, 1182, 1159, 1128, 1109, 1068, 1027, 1001, 907, 842, 812, 755, 699, 538  $\text{cm}^{-1}$ . Elemental analysis calcd. for  $(\text{C}_8\text{H}_8)_{586}(\text{C}_3\text{H}_3\text{O}_2)_{55}(\text{C}_{21}\text{H}_{17}\text{N}_5\text{PtCl})_{55}$ : C 74.79, H 6.06, N 4.00. Found: C 74.86, H 6.27, N 3.87. According to the procedure for the preparation of SAP-1, SAP-2 was prepared with  $[\text{Pt}(\text{tpy})\text{Cl}]^+\text{Cl}^-$  instead of  $[\text{Pt}(\text{Me}_2\text{bzimpy})\text{Cl}]^+\text{Cl}^-$ . IR (KBr): 3079, 3058, 3024, 3000, 2920, 2849, 1942, 1872, 1799, 1721, 1656, 1640, 1622, 1601, 1578, 1563, 1548, 1526, 1492, 1452, 1399, 1378, 1318, 1260, 1180, 1157, 1114, 1068, 1028, 980, 941, 907, 842, 754, 698, 538  $\text{cm}^{-1}$ .  $(\text{C}_8\text{H}_8)_{586}(\text{C}_3\text{H}_3\text{O}_2)_{55}(\text{C}_{15}\text{H}_{11}\text{N}_3\text{Pt})_{27}\text{Na}(\text{C}_{15}\text{H}_{11}\text{Cl}_2\text{N}_3\text{Pt})_5$ : C 81.06, H 6.64, N 1.70. Found: C 80.71, H 6.72, N 1.24.



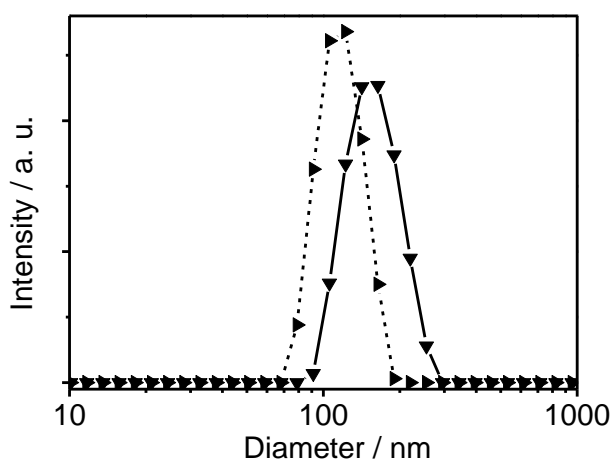
**Fig. S1** Absorption (a) and emission (b and c) spectral changes of  $[\text{Pt}(\text{tpy})\text{Cl}]^+\text{Cl}^-$  (0.4 mmol/L) upon titration of with  $\text{E}_{250}\text{-}b\text{-}A_{51}$  ( $[-\text{COO}^-]/[\text{Pt}(\text{tpy})\text{Cl}]^+ = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, \text{ and } 3.0$ ).



**Fig. S2** The change of the average hydrodynamic diameters ( $D_h$ ) of  $[\text{Pt}(\text{Me}_2\text{bzimpy})\text{Cl}]^+\text{Cl}^-$  (0.4 mmol/L) upon titration of with  $\text{E}_{250-b}\text{-A}_{51}$  ( $[-\text{COO}]/[\text{Pt}(\text{Me}_2\text{bzimpy})\text{Cl}]^+ = 0, 0.2, 0.4, 0.6, 0.8, 1.0,$  and 1.2).



**Fig. S3** Bright-field TEM image of EAP-1 (a). Core width distribution of the rodlike micelles of EAP-1 (b). Bright-field TEM image of EAP-2 (c).



**Fig. S4** DLS plots of the  $D_h$ s of SAP-1 (—) and SAP-2 (---) in toluene.

#### Additional results and discussion.

(1) It would be interesting to understand whether the self-assembly capacity of the polymer has a role in the final supramolecular arrangement.  $\text{E}_{250-b}\text{-A}_{51}$  is soluble in water. Both EAP-1 and EAP-2 formed rodlike micelles in aqueous dispersions. The platinum(II) cations were brought into

close proximity with each other by the A segments, which therefore leads to the insoluble domains stabilized by the E in water. This self-assembly process is in a homogeneous aqueous dispersion and thus is believed to be in a state of thermodynamic equilibrium.

Of difference is that  $S_{586-b-A_{55}}$  is insoluble in water and forms spherical micelles in organic solvents. Both SAP-1 and SAP-2 were prepared in a heterogeneous environment. SAP-1 formed a dominant morphology of rodlike micelles along with a few spherical micelles and vesicles in toluene and SAP-2 formed spherical micelles in toluene, which were very different from those of EAP-1 and EAP-2. Although  $E_{250-b-A_{51}}$  and  $S_{586-b-A_{55}}$  have different lengths of the neutral blocks, we cannot exclude the possibility of a kinetic control for the morphologies of SAP-1 and SAP-2 during the heterogeneous ionic exchange process. To discuss the detailed mechanism of these aggregates, we will prepare various luminescent polymeric hybrids with changing the relative lengths of the blocks and the total block copolymer molecular weight and then measure their morphological evolution in toluene dispersions.

(2) Our research raises an interesting question for the pH influence of the self-assembly of platinum(II) complexes with the block copolymers in aqueous solution. The pH of the aqueous solution during titration is about 6. When the pH value decreased to 5, the absorption intensity decreased suddenly, and reached a minimum of ca. 0.135. The value of ca. 0.135 at 545 nm corresponded to the state at a  $[-COO^-]/[Pt(Me_2bzimpy)Cl]^+$  molar ratio of 0.4. The absorption intensity cannot return to the original value (ca. 0.102) of the aqueous solution of  $[Pt(Me_2bzimpy)Cl]^+Cl^-$  (0.4 mmol/L) even though the pH value was 2. When the  $A_{51}$  block was about 50% neutralized to acid, the maximum absorbance at 545 nm still saturated at 1. The increase in 80 % neutralization of the  $A_{51}$  block led to a titration inflection point at 2.02. The total neutralization of the  $A_{51}$  block led to an increase of the inflection point to 2.50.

Our results were very different from those reported by Yam et al (*Angew. Chem. Int. Ed.*, 2005, **44**, 791 and *Chem. Eur. J.* 2009, **15**, 2328). In the case of Yam's work, the self-assembly of the Pt complexes induced by polyelectrolytes is really reversible between the aggregated state and monomeric state via alternate addition of bases and acids in organic solvents. The difference may be attributed to neutral carboxylic acids in organic solvents and partial dissociation of the carboxylic acids into  $H^+$  cations and  $RCOO^-$  anions in aqueous solution.

(3) SAP-1 formed a dominant morphology of rodlike micelles along with a few spherical micelles and vesicles in toluene. SAP-2 formed spherical micelles in toluene. We think that two reasons may be responsive for their morphological difference. The first reason is that  $[Pt(Me_2bzimpy)Cl]^+Cl^-$  have a bigger size than that of  $[Pt(tpy)Cl]^+Cl^-$ , which leads to the larger increase in both the hydrophilic volume fraction and the interfacial tension between the ionic species and the toluene/S blocks. The second one is that SAP-1 has a molar ratio of 1:1 between the  $[Pt(Me_2bzimpy)Cl]^+$  cation and the acrylate of  $S_{586-b-A_{55}}$ , while SAP-2 have a molar ratio of 1:2 between the Pt complex and the acrylate of  $S_{586-b-A_{55}}$ , which would be a charge ratio effect.

**Complete reference 1** (Ref. 1b, 1c and 1d have been deleted because of the limited pages of the manuscripts):

- 1 (a) V. M. Miskowski and V. H. Houlding, *Inorg. Chem.*, 1989, **28**, 1529. (b) V. M. Miskowski and V. H. Houlding, *Inorg. Chem.*, 1991, **30**, 4446. (c) W. B. Connick, L. M. Henling, R. E. Marsh and H. B. Gray, *Inorg. Chem.*, 1996, **35**, 6262. (d) W. B. Connick, D. Geiger, and R. Eisenberg, *Inorg. Chem.*, 1999, **38**, 3264. (e) F. N. Castellano, I. E. Pomestchenko, E. Shikhova, Fei Hua, M. L. Muro and Nepali Rajapakse, *Coord. Chem. Rev.*, 2006, **250**, 1819. (f) W. Lu, B. X. Mi, M. C. W.

Chan, Z. Hui, C. M. Che, N. Zhu and S. T. Lee, *J. Am. Chem. Soc.* 2004, **126**, 4958. (g) W. Lu, Y. Chen, V. A. L. Roy, S. S.-Y. Chui and C.-M. Che, *Angew. Chem., Int. Ed.*, 2009, **48**, 7621. (h) J. A. G. Williams, S. Develay, D. L. Rochester and L. Murphy, *Coord. Chem. Rev.*, 2008, **252**, 2596.

## References

1. L. J. Grove, J. M. Rennekamp, H. Jude and W. B. Connick, *J. Am. Chem. Soc.*, 2004, **126**, 1594.
2. (a) Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* 1934, 1498. (b) Howe-Grant, M.; Lippard, S. *J. Inorg. Synth.* 1980, **20**, 101.