Electronic Supplementary Information (ESI) for

Composites of Quaternized Poly(pyridylacetylene) and Silver Nanoparticles: Nanocomposite Preparation, Conductivity and Photoinduced Patterning

Yu Mao,^a Hai Peng Xu,^a Hui Zhao,^a Wang Zhang Yuan,^{a, b} Anjun Qin,^a Yong Yu,^b Mahtab Faisal,^b Xiao A Zhang,^a Jing Zhi Sun,^{*, a} and Ben Zhong Tang ^{* a, b}

^a MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China; ^b Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China.

* To whom correspondence should be addressed. E-mail: <u>sunjz@zju.edu.cn</u>, <u>tangbenz@ust.hk</u>.

Table of Contents

- **Fig. S1** FT-IR spectra of the monomer PyA (A), its polymer PPyA (B), the quaternized resultant PPyA-MI (C) and PPyA-MBr (D). (2)
- **Fig. S2** ¹H NMR spectra of the monomer PyA in chloroform-*d* (A), model compound PyA-MI in D₂O (B), the polymer PPyA in chloroform-*d* (C), and the quaternized polymer PPyA-MI in DMSO- d_6 (D), and PPyA-MBr in DMSO- d_6 (E). The solvent peaks are marked with asterisks. (3)
- **Fig. S3** ¹³C NMR spectra of (A) PyA, (B) its polymer PPyA in chloroform-*d*, (C) PPyA-MI in DMSO*d*6 and (D) PPyA-MBr in D₂O. The solvent peaks are marked with asterisks. (4)
- **Fig. S4** Absorption spectra of PyA in DCM, PPyA in DCM, PPyA-MI and PPyA-MBr in DMSO, $PPyA-MeBr^{-}[Ag(NH_3)_2]NO_3$ in water. Polymer and monomer concentration: 10^{-4} mol/L. (5)
- Fig. S5 Emission spectra of PPyA (in DCM and methanol) and PPyA-MI (in water). (Concentration: 10^{-4} M). (6)
- Fig. S6 Surface elementary analysis data of the casting film of PPyA-MBr/ [Ag(NH₃)₂]NO₃ composite after exposure to UV-light for 6 hours. (7)



Fig. S1 FT-IR spectra of the monomer PyA (A), its polymer PPyA (B), the quaternized resultant PPyA-MI (C) and PPyA-MBr (D).

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry This journal is $\ensuremath{\mathbb{O}}$ The Royal Society of Chemistry 2011



Fig. S2 ¹H NMR spectra of the monomer PyA in chloroform-*d* (A), model compound PyA-MI in D₂O (B), the polymer PPyA in chloroform-*d* (C), and the quaternized polymer PPyA-MI in DMSO- d_6 (D), and PPyA-MBr in DMSO- d_6 (E). The solvent peaks are marked with asterisks.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry This journal is $\ensuremath{\mathbb{O}}$ The Royal Society of Chemistry 2011





Fig. S3 ¹³C NMR spectra of (A) PyA, (B) its polymer PPyA in chloroform-d, (C) PPyA-MI in DMSO-d6 and (D) PPyA-MBr in D₂O. The solvent peaks are marked with asterisks.



Fig. S4 Absorption spectra of PyA in DCM, PPyA in DCM, PPyA-MI and PPyA-MBr in DMSO, PPyA-MeBr- $[Ag(NH_3)_2]NO_3$ in water. Polymer and monomer concentration: 10^{-4} mol/L.

In Figure S4, the UV-vis absorption spectra of monomer PyA, polymer PPyA and quaternized resultans PPyA-MI and PPyA-MBr are displayed. The monomer shows a peak at around 273 nm, which can be assigned to the π - π * transition absorption of pyridine moiety. Meanwhile, the monomer displays very weak absorption beyond 300 nm. But its polymer PPyA has an absorption maximum at around 400 nm and the absorption band extends beyond 500 nm. The red-shifted and broadened absorption band is ascribed to the formation of conjugated polyene backbone and the existence of different conjugation lengths. After quaternization, both PPyA-MI and PPyA-MBr demonstrate further red-shifted absorption spectra with a pronounced absorption band peaked at around 460 nm. These absorption features are reasonably accounted for the better electronic conjugation of polyene main chain and quaternized pyridyl moieties. The absorption spectrum of the hybrid in water exhibits a blue-shifted band peaked at around 410 nm. This blue-shifted absorption feature may be associated with the interactions between Ag⁺ species and polymer, which leads to shorter conjugation lengths of polyene backbone.



Fig. S5 Emission spectra of the solutions of PPyA in DCM and methanol, PPyA-MI in water. (Concentration: 10^{-4} M).



Fig. S6 Surface elementary analysis data of the casting film of PPyA-MBr/ [Ag(NH₃)₂]NO₃ composite after exposure to UV-light for 6 hours.