Supporting Information for:

## A Multifunctional Block Copolymer – Where Polymetallic and Polyelectrolyte Blocks Meet

Mahboubeh Hadadpour<sup>1</sup>, Jessica Gwyther<sup>2</sup>, Ian Manners<sup>2</sup> and Paul J. Ragogna<sup>\*1</sup>

<sup>1</sup>Department of Chemistry and the Centre for Materials and Biomaterials Research (CAMBR), *The* University *of* Western Ontario, London, Ontario, N6A 5B7, Canada <sup>2</sup>School of Chemistry, University of Bristol, Cantocks Close, Bristol, BS8 1TS, UK \*pragogna@uwo.ca

## Table of Content:

**Figure S.I.1.** <sup>1</sup>H NMR Spectrum of random copolymer **5** (spectrum A) and a block copolymer consist of random copolymer **5** and monomer **6** (spectrum B) in deutrated chloroform. In Spectrum B, arrows point to the broad/overlapping signals of polyelectrolyte block. (\*trace of DCM).

Figure S.I.2. Positive and negative mass spectroscopy of purified 7......4

Figure S.I.3. <sup>1</sup>H NMR Spectrum of purified RAFT agent 8 in deutrated chloroform......5

**Figure S.I.4.** <sup>1</sup>H NMR spectrum of crude random copolymer **9** at 20 minutes polymerization reaction time in deutrated chloroform. (Relative integrations values indicate 47% monomer conversion)......**5** 

**Figure S.I.8.**  ${}^{31}P{}^{1}H$  NMR Spectra of crude (bottom) and purified (top) (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf) (10).....7

**Figure S.I.11.**  ${}^{19}F{}^{1}H{}$  NMR Spectrum of purified (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf)<sub>44</sub> (10) after 45 minutes polymerization reaction time in deutrated chloroform.

Figure S.I.15.  ${}^{19}F{}^{1}H{}$  NMR Spectrum of purified (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf)<sub>100</sub> (10).....10

**Figure S.I.16.** TEM Image of spherical micelles made by injection of THF solution of (PolyCpCoCb<sub>50</sub>-r-PMA<sub>150</sub>)-b-(PS( $P^+OTf$ )<sub>100</sub> (**10**) into methanol and size distribution analysis based on TEM data.....**11** 

**Figure S.I.17**. DLS analysis of spherical micelles made by injection of THF solution of (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS( $P^+OTf$ )<sub>100</sub> (**10**) into methanol (130 nm). .....**11** 

**Figure S.I.19.** DLS analysis of heterobimetallic micelles made by injection of DCM solution of (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>AuCl<sub>4</sub><sup>-</sup>))<sub>100</sub> into benzene (65 nm)......12

**Figure S.I.20.** Heterobimetallic micelles with Poly-7AuCl core and PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub> corona made by injection of DCM solution of (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>AuCl<sub>4</sub><sup>-</sup>))<sub>m</sub> (1; m=30, 2; m=100) into benzene. Vials on top are the same micelles samples after the core is reduced to AuNPs using NaBH<sub>4</sub> (3; m=30, 4; m=100) .....12

 Figure S.I.22. EDX analysis of AuNPs (copper signals are form the copper grid)......13

**Figure S.I.23.** A) TEM image of microtomed section of phase separated (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf<sup>-</sup>))<sub>30</sub> stained with RuO<sub>4</sub> B) and stained with HAuCl<sub>4</sub>.

**Figure S.I.24.** EDX analysis of microtomed sections of (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf))<sub>30</sub> stained by RuO<sub>4</sub> revealing its elemental composition......**14** 

**Figure S.I.25.** TEM image (left) and EDX analysis (right) of pyrolyzed (PolyCpCoCb<sub>50</sub>*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf<sup>-</sup>))<sub>30</sub> block copolymer ......15



**Figure S.I.1.** <sup>1</sup>H NMR Spectrum of random copolymer **5** (spectrum A) and a block copolymer consist of random copolymer **5** and polymerized **6** (spectrum B) in deutrated chloroform. In Spectrum B, arrows point to the broad/overlapping signals of the polyelectrolyte block. (\*trace of DCM).



Note: Clusters with Cl such as 637 (2 cation + 1 Cl<sup>-</sup>), 1027 (3 cation + 2 Cl<sup>-</sup>) were not detected.



Note: Clusters with Cl such as 743 (2 cation + 3 Cl<sup>-</sup>), 1099 (3 cation + 4 Cl<sup>-</sup>) were not detected. **Figure S.I.2.** Positive and negative mass spectroscopy of purified **7**.



Figure S.I.3. <sup>1</sup>H NMR Spectrum of purified RAFT agent 8 in deutrated chloroform.



**Figure S.I.4.** <sup>1</sup>H NMR spectrum of crude random copolymer **9** at 20 minutes polymerization reaction time in deutrated chloroform. (Relative integrations values indicate 47% monomer conversion)



**Figure S.I.5.** <sup>1</sup>H NMR spectrum of crude random copolymer **9** at 40 minutes polymerization reaction time in deutrated chloroform. (Relative integrations values indicate 77% monomer conversion)



**Figure S.I.6.** <sup>1</sup>H NMR spectrum of crude random copolymer **9** at 60 minutes polymerization reaction time in deutrated chloroform. (Relative integrations values indicate 82% monomer conversion)



**Figure S.I.7.** <sup>1</sup>H NMR spectrum of purified PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub> random copolymer (9) at 60 minutes polymerization reaction time.



**Figure S.I.8.** <sup>31</sup>P{<sup>1</sup>H} NMR Spectra of crude (bottom) and purified (top) (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf) (10)



**Figure S.I.9.** <sup>19</sup>F ${^{1}H}$  NMR Spectrum of purified (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf)<sub>20</sub> (10) after 15 minutes polymerization reaction time in deutrated chloroform.



**Figure S.I.10.** <sup>19</sup>F{<sup>1</sup>H} NMR Spectrum of purified (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf)<sub>33</sub> (10) after 30 minutes polymerization reaction time in deutrated chloroform.



**Figure S.I.11.** <sup>19</sup>F $\{^{1}H\}$  NMR Spectrum of purified (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf)<sub>44</sub> (10) after 45 minutes polymerization reaction time in deutrated chloroform.



**Figure S.I.12.** <sup>19</sup>F $\{^{1}H\}$  NMR Spectrum of purified (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf) <sub>50</sub> (10) after 60 minutes polymerization reaction time in deutrated chloroform.



**Figure S.I.13.** <sup>1</sup>H NMR spectrum of purified block copolymer **10** after 60 minutes polymerization reaction time. Arrows show broad signals of polyelectrolyte block in deutrated chloroform. (\*Residue of dichloromethane)



Figure S.I.14. <sup>19</sup>F {<sup>1</sup>H} NMR Spectrum of purified (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf)<sub>30</sub> (10).



Figure S.I.15. <sup>19</sup>F $\{^{1}H\}$  NMR Spectrum of purified (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf)<sub>100</sub> (10).



**Figure S.I.16.** TEM Image of spherical micelles made by injection of THF solution of (PolyCpCoCb<sub>50</sub>-r-PMA<sub>150</sub>)-b-(PS( $P^+OTf$ )<sub>100</sub> (**10**) into methanol and size distribution analysis based on TEM data.



**Figure S.I.17**. DLS analysis of spherical micelles made by injection of THF solution of (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf)<sub>100</sub> (**10**) into methanol (130 nm).



**Figure S.I.18.** TEM Image of heterobimetallic micelles made by injection of DCM solution of (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS( $P^+AuCl_4^-$ ))<sub>100</sub> into benzene and size distribution analysis based on TEM data.



**Figure S.I.19.** DLS analysis of heterobimetallic micelles made by injection of DCM solution of (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS( $P^+AuCl_4^-$ ))<sub>100</sub> into benzene (65 nm).



**Figure S.I.20.** Heterobimetallic micelles with Poly-7AuCl core and PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub> corona made by injection of DCM solution of (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>AuCl<sub>4</sub><sup>-</sup>))<sub>m</sub>(1; m=30, 2; m=100) into benzene. Vials on top are the same micelles samples after the core is reduced to AuNPs using NaBH<sub>4</sub>(3; m=30, 4; m=100).



**Figure S.I.21.** TEM Image of AuNPs made by reduction of heterobimetallic micelles made  $[(PolyCpCoCb_{50}-r-PMA_{150})-b-(PS(P^+AuCl_4^-))_m]$  and size distribution analysis based on TEM data.



Figure S.I.22. EDX analysis of AuNPs (copper signals are form the copper grid).



**Figure S.I.23.** A) TEM image of microtomed section of phase separated (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf<sup>-</sup>))<sub>30</sub> stained with RuO<sub>4</sub> B) and stained with HAuCl<sub>4</sub>.



**Figure S.I.24.** EDX analysis of microtomed sections of  $(PolyCpCoCb_{50}-r-PMA_{150})-b-(PS(P^+OTf))_{30}$  stained by RuO<sub>4</sub> revealing its elemental composition.



Figure S.I.25. TEM image (left) and EDX analysis (right) of pyrolyzed (PolyCpCoCb<sub>50</sub>-*r*-PMA<sub>150</sub>)-*b*-(PS(P<sup>+</sup>OTf<sup>-</sup>))<sub>30</sub> block copolymer .



Figure S.I.26. The pyrolyzed materials were attracted to permanent magnet, indicating the presence of magnetic particles.