Supporting Information

Ultra Metal Ions and pH Sensing Characteristics of Thermoresponsive Luminescent Electrospun Nanofibers Prepared From Poly(HPBO-*co*-NIPAAm-*co*-SA)

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Synthesis of 4-(6-hydroxyhexyloxy)-2-hydroxybenzaldehyde (1)

2g of 6-bromoethanol (11 mmol)、1.53g potassium carbonate (11 mmol)、1.53g 2,4-dihydroxy (11 mmol) in 50 mL acetone was refluxed at 65 °C under nitrogen atmosphere for 24 hrs. After extraction with 10 wt% Na_2CO_3、water and saturated brine, dried over $MgSO_4$ and the solvent was removed under vacuum. The crude was passed through a silica gel column with hexane : acetone = 2 : 1 as eluent. Then recrystallization from hexane : acetone = 10 : 1 to get 2.1g white solid compound. Yield is 79%. ^{1}HNMR (d-$CDCl_3$, 400MHz): δ(ppm) = 1.2-1.8 [m, H^8, -($C\underline{H}_2$)$_4$-], 3.6 (t, H^3, -$C\underline{H}_2$OH), 4.0 (t, H^2, -O-$C\underline{H}_2$-), 6.4 (s, H^1, phenyl), 6.5 (d, H^1, phenyl) , 7.4(d, H^1, phenyl), 9.7 (s, H^1, -C$\underline{H}$O), 11.5 (s, H^1, -phenyl-O$\underline{H}$).

Synthesis of 4-(6-(methoxymethoxy)hexyloxy)-2-(methoxymethoxy) benzaldehyde (2)

2g of compound **1** (8.4 mmol) was dissolved into 15ml of dry methylene chloride and 5.2ml of *N*-ethyl-diisopropylamine (30 mmol). Then 1.6ml of chloro methyl ether (21 mmol) was added in this solution at 0 °C. The mixture was stirred at room temperature for 15 hrs. After extraction with 5% $NaHCO_3$ and saturated brine, dried over $MgSO_4$ and the solvent was removed under vacuum to get 2.46g yellow oil product. Yield is 90%. ^{1}HNMR (d-$CDCl_3$, 400MHz): δ(ppm) = 1.2-1.8 [m, H^8, -($C\underline{H}_2$)$_4$-], 3.4 (s, H^3, $PhOCH_2OC\underline{H}_3$), 3.5 (t, H^2, $CH_3OCH_2OC\underline{H}_2$-), 3.6 (s, H^3, -$OC\underline{H}_3$), 4.0 (t, H^2, Ph-O-$C\underline{H}_2$-CH_2-), 4.6 (s, H^2,

$CH_3OC\underline{H}_2OCH_2$-), 5.3 (s, H^2, Ph-O-$C\underline{H}_2$-OCH_3), 6.6 (d, H^1, phenyl), 6.7 (s, H^1, phenyl) , 7.8(d, H^1, phenyl), 10.3 (s, H^1, -C$\underline{H}$O).

Synthesis of 2-(4-(6-(methoxymethoxy)hexyloxy)-2-(methoxymethoxy)phenyl) benzo xazole (3)

5.37g of compound **2** (16.5 mmol)、1.8g of 2-aminophenol (16.5 mmol) was dissolved into 100 mL of benzene and refluxed for 15hrs. Then 10.54 g of $BaMnO_4$ was added into the mixture and refluxed for 24hrs. Inorganic salt $BaMnO_4$ was removed through by filtration of Celite. After extraction with 10 wt% Na_2CO_3、water and saturated brine, dried over $MgSO_4$ and the solvent was removed under vacuum. The crude was passed through a silica gel column with methylene chloride : ethyl acetate = 1 : 1 as eluent to get 2.1g yellow oil compound. Yield is 31%. ^{1}HNMR (d-$CDCl_3$, 400MHz): δ(ppm) = 1.2-1.8 [m, H^8, -($C\underline{H}_2$)$_4$-], 3.4 (s, H^3, $PhOCH_2OC\underline{H}_3$), 3.5 (t, H^2, $CH_3OCH_2OC\underline{H}_2$-), 3.6 (s, H^3, -$OC\underline{H}_3$), 4.0 (t, H^2, Ph-O-$C\underline{H}_2$-CH_2-), 4.6 (s, H^2, $CH_3OC\underline{H}_2OCH_2$-), 5.3 (s, H^2, Ph-O-$C\underline{H}_2$-OCH_3), 6.6 (m, H^1, phenyl), 6.8 (s, H^1, phenyl), 7.3 (m, H^2, phenyl), 7.6 (m, H^1, phenyl), 7.9(d, H^1, phenyl), 8.1 (d, H^1, phenyl).

Synthesis of 5-(6-hydroxyhexyloxy)-2-(benzoxazol-2-yl)phenol (4)

1.1g of compound **3** (2.6 mmol) was dissolved into 65 mL of methanol and 1.1g of p-toluene sulfonic acid was added into this solution. The mixture was stirred at room temperature for 48 hrs. After removing the solvent, the remaining crude was dissolved into methylene chloride. Then washed with 5% $NaHCO_3$、water and saturated brine, dried over $MgSO_4$. The crude was passed through a silica gel column with methylene chloride : methanol = 15 : 1 as eluent to get 0.61g orange powder compound. Yield is 72%. ^{1}HNMR (d-$CDCl_3$, 400MHz): δ(ppm) = 1.2-1.8 [m, H^8, -(C$\underline{H}_2$)$_4$-], 3.4 (s, H^3, PhOCH$_2$OC$\underline{H}_3$), 3.6 (t, H^2, HOC$\underline{H}_2$-), 4.0 (t, H^2, Ph-O-C$\underline{H}_2$-CH$_2$-), 6.5 (m, H^1, phenyl), 7.3 (m, H^2, phenyl), 7.5 (m, H^1, phenyl), 7.7(d, H^1, phenyl), 11.6 (s, H^1, phenyl-O$\underline{H}$).

Synthesis of 2-{2-hydroxyl-4-[5-(acryloxy)hexyloxy]phenyl}benzoxazole (5)

450mg of compound **4** (1.37 mmol)、100mg of acrylic acid (1.37 mmol)、316mg of EDC (1.64 mmol) and 17mg of 4-dimethylaminopyridine (0.137 mmol) was dissolved into 6 mL of methylene chloride and the mixture was stirred at room temperature for 48 hrs. After removing the solvent, the crude was passed through a silica gel column with methylene chloride : methanol = 20 : 1 as eluent to get 0.198g yellow powder compound. Yield is 38%. ^{1}HNMR (d-$CDCl_3$, 400MHz): δ(ppm) = 1.2-1.8 [m, H^8, -(C$\underline{H}_2$)$_4$-], 4.0 (t, H^2, PhOC$\underline{H}_2$-), 4.2 (t, H^2, -OCOC$\underline{H}_2$-), 5.8 (d, H^1, C$\underline{H}_2$=C$\underline{H}$-), 6.1 (m, H^1, C$\underline{H}_2$=C$\underline{H}$-), 6.5 (d, H^1, C$\underline{H}_2$=C$\underline{H}$-), 7.3

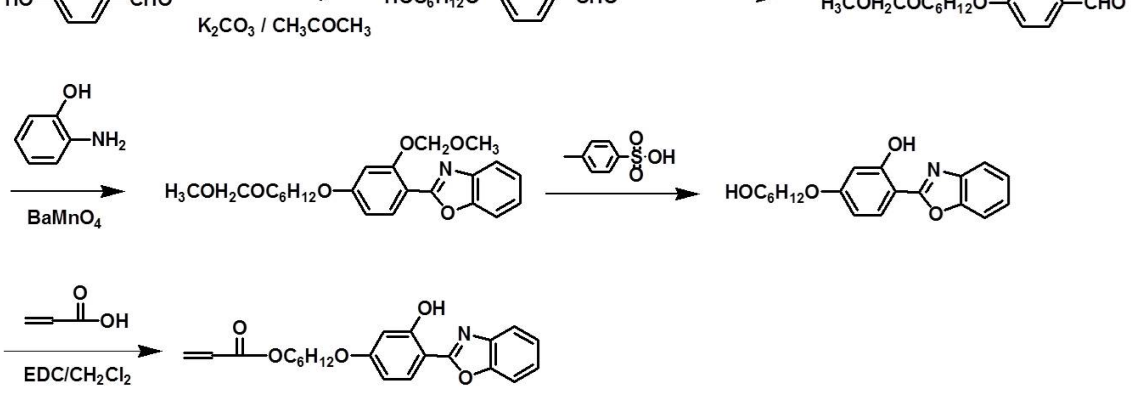
(m, H^2, phenyl), 7.5 (m, H^1, phenyl), 7.7 (m, H^1, phenyl), 7.9 (d, H^1, phenyl), 11.6 (m, H^1, phenyl-O<u>H</u>).

Synthesis of P1: 7.9mg of HPBO (0.021 mmole), 2.26g of NIPAAm (20 mmole), 0.20g of SA (0.62 mmole), 8.2mg of AIBN (0.05 mmole) were dissolved in 7 mL ethanol and react for 2 days to obtain white solid in 62% yield. ^{1}HNMR (d-CD_2Cl_2, 400MHz): δ(ppm) = 0.8-2.5 [m, H^{58}, -O-CH_2 ($C\underline{H}_2$)$_{16}$-$C\underline{H}_3$, -NH-CH-($C\underline{H}_3$)$_2$, -$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-$C\underline{H}$-, -OCH_2-($C_4\underline{H}_8$)-CH_2O-], 4.0 [m, H^7, -O$C\underline{H}_2$-(C_4H_8)-$C\underline{H}_2$O-, -NH-$C\underline{H}$-(CH_3)$_2$, -O-$C\underline{H}_2$-(CH_2)$_{16}$-CH_3], 6.2-7.1 [m, H^1, -N<u>H</u>-CH-(CH_3)$_2$], 7.1-7.9 (m, H^7, phenyl). Elemental Anal. Calcd for **P1**: C, 65.34; H, 9.19; N, 9.19. Found: C, 64.16; H, 9.01; N, 12.32.

Synthesis of P2 : 243mg of HPBO (0.063 mmole), 2.26g of NIPAAm (20 mmole), 0.21g of SA (0.64 mmole), 8.2mg of AIBN (0.05 mmole) were dissolved in 7 mL ethanol and react for 2 days to obtain white solid in 62% yield. ^{1}HNMR (d-CD_2Cl_2, 400MHz): δ(ppm) = 0.8-2.5 [m, H^{58}, -O-CH_2 ($C\underline{H}_2$)$_{16}$-$C\underline{H}_3$, -NH-CH-($C\underline{H}_3$)$_2$, -$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-$C\underline{H}$-, -OCH_2-($C_4\underline{H}_8$)-CH_2O-], 4.0 [m, H^7, -O$C\underline{H}_2$-(C_4H_8)-$C\underline{H}_2$O-, -NH-$C\underline{H}$-(CH_3)$_2$, -O-$C\underline{H}_2$-(CH_2)$_{16}$-CH_3], 6.2-7.1 [m, H^1, -N<u>H</u>-CH-(CH_3)$_2$], 7.1-7.9 (m, H^7, phenyl). Elemental Anal. Calcd for **P2**: C, 65.78; H, 8.93; N, 10.74. Found: C, 64.35; H, 9.56; N, 11.76.

Synthesis of P3 : 2.26g of NIPAAm (20 mmole), 0.414g of SA (1.28 mmole), 8.2mg of AIBN (0.05 mmole) were dissolved in 7 mL ethanol and react for 3 days to obtain white solid in 62% yield. ^{1}HNMR (d-CD_2Cl_2, 400MHz): δ(ppm) = 0.8-2.5 [m, H^{58}, -O-CH_2 ($C\underline{H}_2$)$_{16}$-$C\underline{H}_3$, -NH-CH-($C\underline{H}_3$)$_2$, -$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-$C\underline{H}$-, -OCH_2-($C_4\underline{H}_8$)-CH_2O-], 4.0 [m, H^7, -$OC\underline{H}_2$-(C_4H_8)-$C\underline{H}_2O$-, -NH-$C\underline{H}$-(CH_3)$_2$, -O-$C\underline{H}_2$-(CH_2)$_{16}$-CH_3], 6.2-7.1 [m, H^1, -$N\underline{H}$-CH-(CH_3)$_2$].

Synthesis of P5 : 86mg of HPBO (0.22 mmole), 2.26g of NIPAAm (20 mmole), 0.728g of SA (2.24 mmole), 8.2mg of AIBN (0.05 mmole) were dissolved in 7 mL ethanol and react for 3 days to obtain white solid in 62% yield. ^{1}HNMR (d-CD_2Cl_2, 400MHz): δ(ppm) = 0.8-2.5 [m, H^{58}, -O-CH_2 ($C\underline{H}_2$)$_{16}$-$C\underline{H}_3$, -NH-CH-($C\underline{H}_3$)$_2$, -$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-$C\underline{H}$-, -OCH_2-($C_4\underline{H}_8$)-CH_2O-], 4.0 [m, H^7, -$OC\underline{H}_2$-(C_4H_8)-$C\underline{H}_2O$-, -NH-$C\underline{H}$-(CH_3)$_2$, -O-$C\underline{H}_2$-(CH_2)$_{16}$-CH_3], 6.2-7.1 [m, H^1, -$N\underline{H}$-CH-(CH_3)$_2$], 7.1-7.9 (m, H^7, phenyl). Elemental Anal. Calcd for **P4**: C, 67.64; H, 9.66; N, 9.27. Found: C, 65.35; H, 9.34; N, 10.16.



Scheme S1. Synthesis of the HPBO monomer

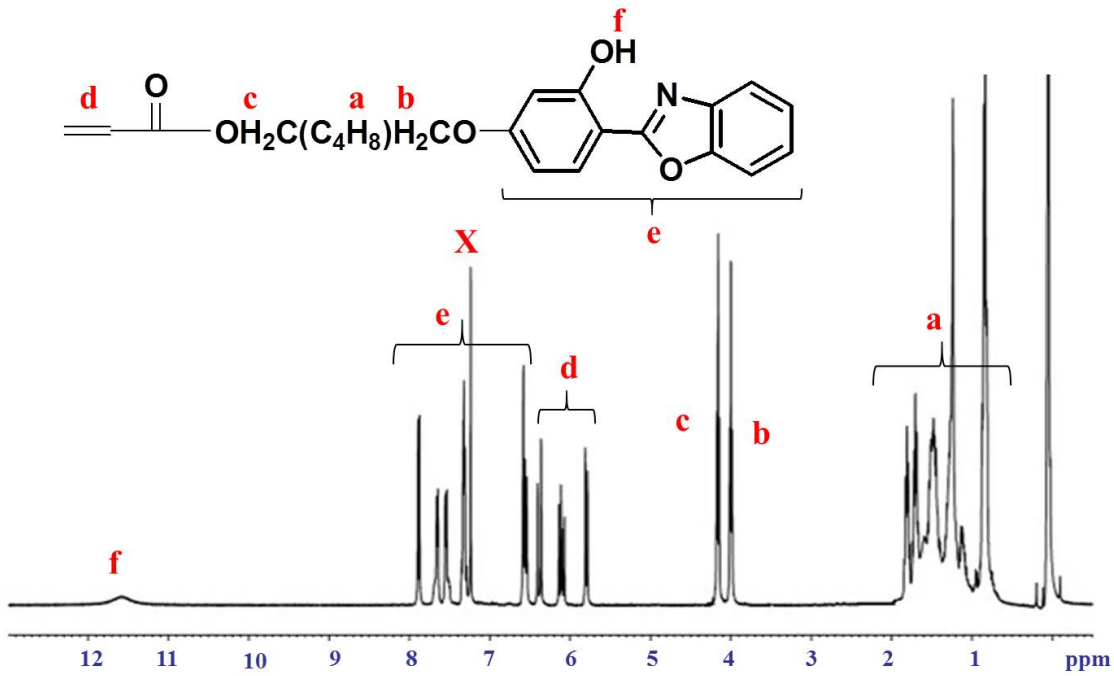


Figure S1. ^{1}H NMR spectrum of HPBO in $CDCl_3$

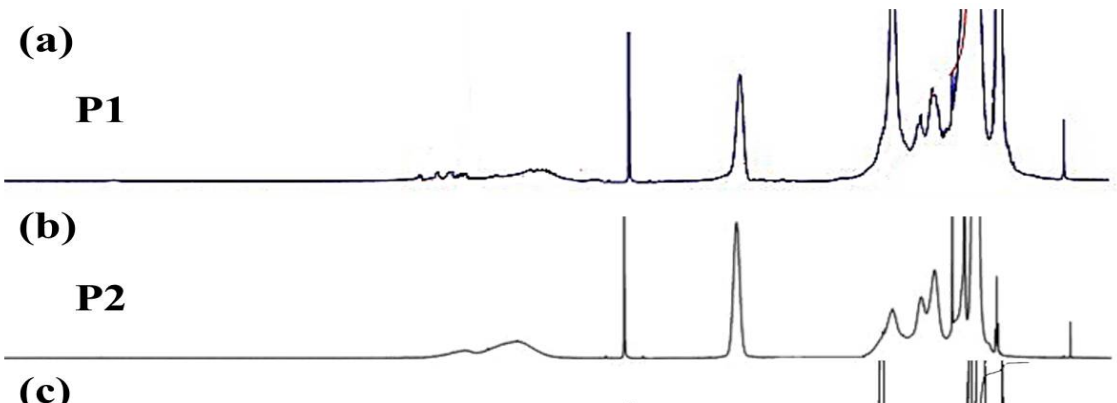


Figure S2. ^{1}H NMR spectra of **P1, P2, P3,** and **P5** in CD_2Cl_2.

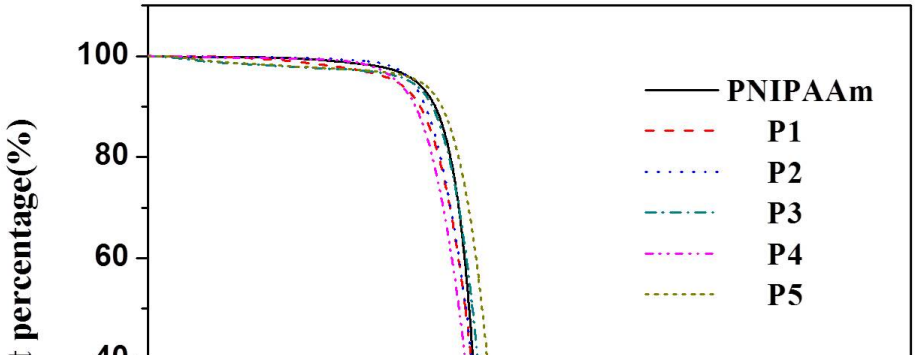


Figure S3. TGA curves of copolymers, **P1**-**P5** under a nitrogen atmosphere.

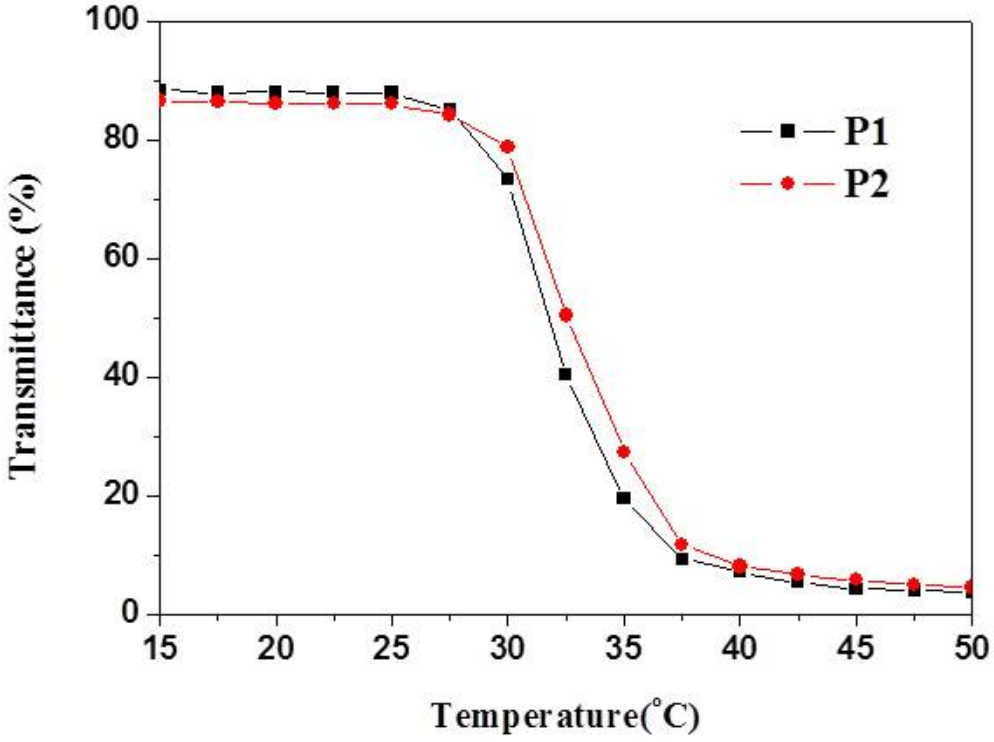


Figure S4. LCSTs of **P1** and **P2** measured by optical transmittance spectra.

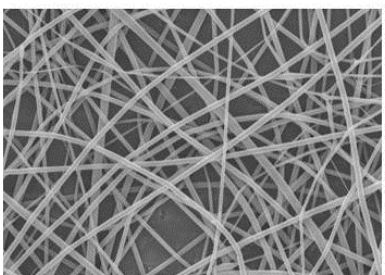
	Dry state	Immersed in water
P1		

Figure S5. The SEM image of the prepared **P1** and **P2** ES nanofibers

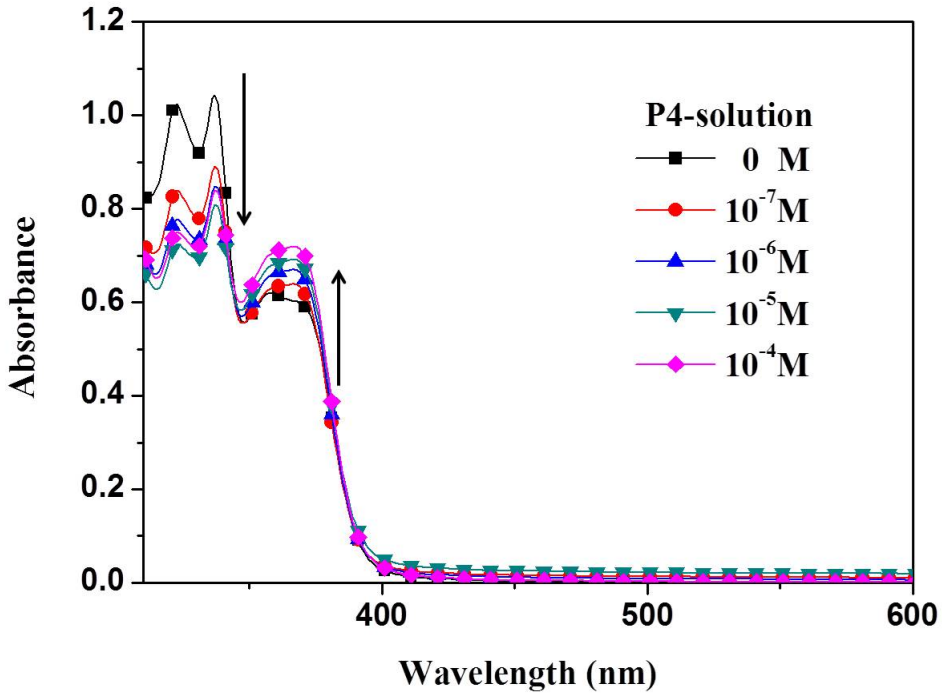
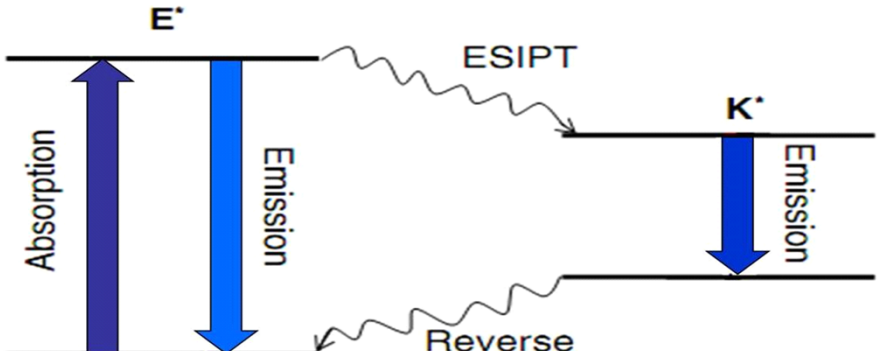


Figure S6. Variation on the UV-Vis absorption spectra for **P4** in THF solution with different Zn^{2+} concentrations.



Scheme S2. ESIPT process and energy level diagram.