Controllable Synthesis of Quantum-Dot-Polymer Networks with Enhanced Luminescence via Catalytic Chain Transfer Polymerization (CCTP) Technique

ShengYang Yang, Qing Li, Li Chen and Su Chen*

State Key Laboratory of Material-Oriented Chemical Engineering and College of Chemistry and Chemical Engineering, Nanjing University of Technology, No. 5 Xin Mofan Rd., Nanjing, JiangSu 210009 (P.R. China)

Measurement details of polymeric ligands

Table S1. GPC data of PMAA oligomers and its block copolymers PMAA-b-PBA

<table>
<thead>
<tr>
<th>Samples</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMAA</td>
<td>2336</td>
<td>2486</td>
<td>1.064212</td>
</tr>
<tr>
<td>PMAA-b-PBA (PMAA : PBA = 70 : 30 wt/wt)</td>
<td>2746</td>
<td>3162</td>
<td>1.151493</td>
</tr>
<tr>
<td>PMAA-b-PBA (PMAA : PBA = 60 : 40 wt/wt)</td>
<td>3387</td>
<td>4466</td>
<td>1.318571</td>
</tr>
<tr>
<td>PMAA-b-PBA (PMAA : PBA = 50 : 50 wt/wt)</td>
<td>3363</td>
<td>6010</td>
<td>1.787094</td>
</tr>
</tbody>
</table>

Fig. S1 Molecular weight distribution of PMAA-b-PBA via RAFT (solvent: isopropanol; reaction time:
5 h) a: PMA : PBA = 70 : 30 wt/wt; b: PMAA : PBA = 60 : 40 wt/wt; c: PMAA : PBA = 50 : 50 wt/wt.

Fig. S2 $^1$H NMR (300 MHz, DMF) of poly (methacrylic acid) macromonomer prepared via CCTP with the water resonance reduced by solvent suppression. p: vinyl protons in the product; m: vinyl protons in the monomer. (solvent: DI water; reaction time: 1 h).

Fig. S3 Raman shift spectra of (a) PMAA prepared via free radical polymerization (solvent: H$_2$O, reaction time: 5h) (b) via CCTP (solvent: H$_2$O, reaction time: 1h); (c) PMAA-b-PBA block copolymer prepared via RAFT (solvent: 2-propanol, reaction time: 5 h).

The Raman shift 1640 cm$^{-1}$ indicates the unsaturated carbon-carbon double bonds in end-groups of long chain polymer, which demonstrates CCTP and RAFT processes are very effective to control the structure of polymers.
Scheme S1. Structure of cobalt catalyst CoBF

UV–vis and fluorescence measurements of a series of CdS NCs by varying molar ratios of the polymeric ligand to cadmium acetate (-COOH/Cd$^{2+}$)

**Fig. S4** UV–vis absorption spectra of CdS nanoparticles stabilized by PMAA (a: -COOH/Cd$^{2+}$ = 4/1 mol/mol; b: -COOH/Cd$^{2+}$ = 5/1 mol/mol; c: -COOH/Cd$^{2+}$ = 6/1 mol/mol) and PMAA-b-PBA block copolymers (d: -COOH/Cd$^{2+}$ = 3/1 mol/mol; e: -COOH/Cd$^{2+}$ = 4/1 mol/mol; f: -COOH/Cd$^{2+}$ = 5/1 mol/mol) in N, N’-dimethylformamide (DMF) solution of different ratios of -COOH/Cd$^{2+}$ (Cd$^{2+}$/S$^{2-}$ = 1/0.6 mol/mol, solvent: H$_2$O/DMF = 0.2/1.0 wt/wt, reaction time: 2 h).
**Fig. S5** Fluorescence emission spectra of PMAA-stabilized CdS nanocrystals suspension dispersed in DMF of different ratios of -COOH/Cd$^{2+}$ (a: -COOH/Cd$^{2+}$ = 4; b: -COOH/Cd$^{2+}$ = 5; c: -COOH/Cd$^{2+}$ = 6) with excitation at 350 nm (Cd$^{2+}$/S$^{2-}$ = 1/0.6 mol/mol, solvent: H$_2$O/DMF = 0.2/1.0 wt/wt, reaction time: 2 h).

**Fig. S6** Fluorescence emission spectra of PMAA-b-PBA block copolymers (PMAA : PBA = 60 : 40 wt/wt ) stabilized CdS nanocrystals suspension dispersed in DMF of different ratios of -COOH/Cd$^{2+}$ (d: -COOH/Cd$^{2+}$ = 3; e: -COOH/Cd$^{2+}$ = 4; f: -COOH/Cd$^{2+}$ = 5) with excitation at 350 nm (Cd$^{2+}$/S$^{2-}$ = 1/0.6 mol/mol, solvent: H$_2$O/DMF = 0.2/1.0 wt/wt, reaction time: 2 h)