Electronic Supplementary Information (ESI)

Highly stable CsPbBr₃@SiO₂ nanocomposite prepared via confined condensation for use as a luminescent ink

Jin Cai,^a Kailun Gu,^a Yihua Zhu,^{*a} Jingrun Zhu,^a Yuanwei Wang,^a Jianhua Shen,^a Adrian Trinchi,^b Chunzhong Li,^{*a} and Gang Wei^{*c,a}

^aKey Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China.

^bCSIRO Manufacturing, Private Bag 10, Clayton South, VIC 3169, Australia.

^cCSIRO Manufacturing, PO Box 218, Lindfield, NSW 2070, Australia.

*E-mail: <u>yhzhu@ecust.edu.cn</u>.

*E-mail: czli@ecust.edu.cn.

*E-mail: gang.wei@csiro.au.

Experimental

Materials

All reagents were of analytical grade and used as received without further purification. Glutaric Anhydride, CsBr, PbBr₂, PbCl₂, PbI₂, bis[3-(triethoxysilyl)propyl] amine and aminopropyltriethoxysilane (APTES), tetrabutylammonium iodide (TBAI) were ordered from Sahn chemical technology (Shanghai) Co Ltd. N, N-Dimethylformamide (DMF), Tetrahydrofuran (THF), methylene chloride (DCM), hydrobromic acid (HBr, 48wt % in water), Tetrabutylammonium hydroxide (TBAOH, 25wt % in water), polystyrene (PS) were obtained from Shanghai Lingfeng Chemical Reagent Co Ltd. All the chemical reagents were purchased as high purity (AR grade) and used without any further purification.

Synthesis of compound BTPA-GA

Glutaric anhydride (2.28 g, 20 mmol) was dissolved in THF (40 mL), and bis[3-(triethoxysilyl)propyl] amine (8.51 g, 20 mmol) added slowly in succession under stirring. After reacting for 24 h, the red crude product product was extracted using a rotary evaporator, and used without further purification.

Preparation of CPB QDs with organosilicon as ligand

In a typical synthesis of CsPbBr₃ QDs, 0.2 mmol PbBr₂ and 0.1 mmol CsBr was dissolved in 5 mL DMF, along with with 100 μ L of APTES and 0.5 mL of compound BTPA-GA synthesized in the above mentioned experiment. Subsequently, 20 μ L of hydrobromic acid was then injected to form a precursor solution. After stirring 10 min until clarification, 500 μ L of the precursor solution was added drop wise into 15 millilitres of DCM with vigorous stirring. After centrifugation at 10000 rpm for ten minutes to discard precipitate with large size, and the supernatant with bright green fluorescence was retained.

Preparation of CPB@SiO₂ nanocomposites

In this process, 3 g of PS were added into the above CPB QDs solution under vigorous stirring. After stirring for 1 hour to ensure mix uniformity, an appropriate amount of solution, typically 15 mL was dropped to the surface dish and evenly dispersed by shaking until the liquid no longer flowed. The surface dish was subsequently placed in the oven and heated at 100 °C. 12 h later, a CPB@SiO₂/PS film with bright green fluorescence was obtained. Then, the film was dissolved in toluene and washed 3 times to remove PS.

Material characterizations

The XRD patterns were recorded on a D/max2550VB/PC X-ray diffractometer. The morphology and nanostructure was investigated on TEM and HRTEM (JEOL-2100). The infrared spectra (2% sample in KBr pellet) were recorded on a Nicolet 6700 FT-IR spectrometer. The ¹H NMR and ¹³C NMR spectra were obtained on a Brucker DRE AVANCE-400 MHz. The absorption behaviors of the samples were studied by the UV1900 UV-vis spectrometer. Photoluminescence (PL) spectra were scanned on a photoluminescence spectrometer (RF-6000). For all PL QY measurements, the optical density at 365 nm was below 0.1; QY was determined relative to Rhodamine 6G in ethanol (QY = 95%).

Characterization Data

The synthesis scheme is shown in Figure S1.



Figure S1. Scheme of preparation of compound BTPA-GA

¹H NMR (400 MHz, DMSO- d_6) δ 3.75 (h, J = 7.3, 6.9 Hz, 12H), 3.18 (dt, J = 14.7, 7.6 Hz, 4H), 2.28 (t, J = 7.4 Hz, 2H), 2.20 (t, J = 7.4 Hz, 2H), 1.71 (q, J = 7.3 Hz, 2H), 1.59 – 1.41 (m, 4H), 1.14 (td, J = 7.0, 3.3 Hz, 18H), 0.57 – 0.42 (m, 4H). ¹³C NMR (101 MHz, DMSO- d_6) δ **174.44**, **171.04**, 57.77, 57.70, 57.61 for the 3rd 2xCH2, 56.07, 49.67, 47.93, 33.23, 31.45, 22.33, 20.93, 20.69, 18.52, 18.14, 18.06, 7.32, 6.89.



Figure S2. ¹H NMR of compound BTPA-GA.



Figure S3. ¹³C NMR of compound BTPA-GA.



Figure S4. Size distribution of CPB QDs (a) capped with organosilicon as ligand and (b)

encapsulated with silica.



Figure S5. TEM image of CPB after direct heat-treatment without PS.



Figure S6. (a) Survey-scan XPS spectra of CPB@SiO₂. XPS spectra of CPB@SiO₂: (b) Si 2p and (c)

O 1s.



Figure S7. PL spectra of CPB@SiO₂ in DMF solution and that with addition of $PbCl_2$.