Electronic Supplementary Information

Photoluminescent poly(ether ether ketone)-quantum dot composite films

Lijun Zhu[1], Pengfei Huo[2], Qian Wang[1], Fuxin Liang[1], Chengliang Zhang[1], Jiaoli Li[1], Xiaozhong Qu[1*], Guibin Wang[2*], Zhenzhong Yang[1*]

[1] *State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.* [2] *College of Chemistry, Engineering Research Center of High Performance Plastics, Ministry of Education, Jilin University, ChangChun 130012, China.*

[* To whom correspondence should be addressed. Email: quxz@iccas.ac.cn (X.Q.), wgb@jlu.edu.cn (G.W.), yangzz@iccas.ac.cn (Z.Y.)]

Experimental

Materials:

Fluoropoly(ether ether ketone) (FPEEK) (Mn=6 kDa, Mw=8 kDa; T_g=130 °C) was synthesized according to our previous report. [1] CdSe/ZnS core/shell quantum dots (QD) with a maximum emission wavelength of 545 nm (green-emitting) was purchased from Wuhan Jiayuan Quantum Dots Co. Ltd. and dispersed in n-hexane before use. Cadmium oxide (CdO, 98.9%), selenium (99%, powder), sulfur (99.9%, powder) and 1-octadecene (ODE, 90%) were obtained from Aldrich. Zinc acetate (99%, powder), oleic acid (OA, 80%) and trioctylphosphine (TOP, 90%) were purchased from Acros Organics, Merck and Fluka, respectively. Solvents and other compounds were obtained from Beijing Chemical Reagents Co., China.

Synthesis of red-emitting alloyed CdSe/ZnS QDs with chemical composition gradients:

Red-emitting alloyed CdSe/ZnS QD (λ_{ex}=615 nm) with chemical composition gradients was synthesized based on literature. [2] Typically, a mixture of 1 mmol of CdO, 1.5 mmol of Zn(acetate)$_2$ and 3 mL of oleic acid (OA) in a 50 mL flask were degassed, filled with Ar gas (five times) and heated to 180 °C until a pale yellow solution was obtained. Then the temperature was adjusted to 100 °C, followed by the addition of 10 mL of 1-octadecene (ODE) and degassed for 20 min. Subsequently, the temperature was elevated to 300 °C under Ar flow, to yield a clear solution of Cd(OA)$_2$ and Zn(OA)$_2$. At this time, 0.5 mmol of Se dissolved in 1.5 mL of trioctylphosphine (TOP) was swiftly injected into the system and the reaction flask was further heated to 310 °C for the growth of $Cd_{1-x}Zn_xSe$ core. After 10 min, the reaction system was allowed to cool down to 235 °C. And to this 1.8 mmol of sulfur dissolved in 1.2 mL of TOP was swiftly injected and the temperature was elevated again to 260 °C for the growth of ZnS shell. The reaction was stopped after 60 min by removing the heating mantle and the solution was hold at 60 °C. Finally, 10 mL of hexane was added and excess amount of acetone was used for precipitation and washing the QD (twice). The QD was dried under vacuum and redispersed in hexane for future experiments.

Preparation of FPEEK-QD composite films:

Appropriate amount of QD (green-emitting and/or red-emitting) dispersed in n-hexane (10 mg/mL) was pipetted into 5 mL glass vials, and the solvent was evaporated under a nitrogen gas stream. Desired volume of FPEEK toluene solution (50 mg/mL) was added into the vials to gain a required QD content of approximate 1.0-5.0 wt%. The mixture was sonicated in an ultrasonic bath to ensure sufficient wetting and the formation of uniform QDs dispersion in the polymer solution. Then the polymer/QD dispersion was poured into a stainless steel mold. After heating overnight at 60°C, the resultant composite film was detached from the mold. The thickness of the films can be tuned depending on the amount of casting solution and/or the concentration of the FPEEK solution.

***Characterizations*:**

The absorption and transmittance spectra of FPEEK and composite films were collected in the range of 400-700 nm on a TU-1901 UV-Vis spectrophotometer.

The fluorescence spectra of FPEEK and composite films were recorded on an F-4500 fluorescence spectrophotometer on reflection mode with an angle of 40° to the excitation light. The width of both the excitation and emission slits is 5 nm. To measure the temperature sensitivity of the composite films, a film was mounted on an aluminum plate and covered by a piece of quartz glass. A ceramic heating plate and a thermometer were firmly connected to the aluminum plate, which were joined to a temperature controller with an accuracy of ±0.2°C.

The crystallization behavior of the FPEEK film was investigated by Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation (λ=0.154 nm) as the X-ray source. In addition, differential scanning calorimetry (DSC) was performed on a Q2000 DSC instrument in the range of 150-390 °C at a heating/cooling rate of 10 °C/min under nitrogen. Thermogravimetric analysis (TGA) was carried out using Perkin-Elmer Pyris 1 with a heating rate of 10 °C/min, under nitrogen and in air respectively.

AFM images were taken under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in tapping mode. TEM observation was performed on sliced specimen of the composite films using a JEM-1011 microscope at an operating voltage of 100 kV. The film was embedded in epoxy resin and microtomed into slices with a thickness of 80-100 nm using a Leica ultracut UCT ultramicrotome (A-1170 Wien-Austria).

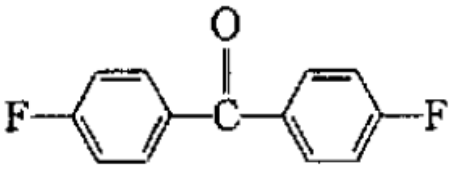
Optical images were gained using a SONY DSC-TX100 camera. For recording the photoluminescence of the films, a UV-Ⅱ UV lamp (6 W) was used to irradiate the films in dark at a wavelength of 365 nm. In order to demonstrate the color change of the FPEEK-QD composite film upon the variation of temperature, a red-emitting QD incorporated film was put on a Linkam LTS 350 thermo-plate and covered by a glass coverslip. Photographs were then taken after the film was equilibrated at predicted temperatures, i.e. 30 and 90 °C.

References:

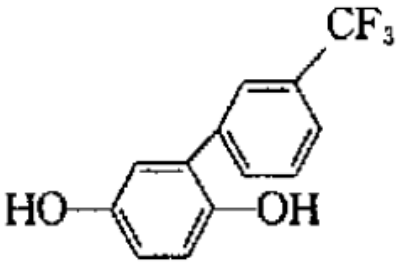
[1] G. B. Wang, C. H. Chen, H. W. Zhou, Z. H. Jiang, W. J. Zhang and Z. W. Wu, *Chem. J. Chin. Univ.-Chin.*, 2000, **21,** 1325.

[2] X. F. Liu, Y. Gao, X. M. Wang, S. J. Wu and Z. Y. Tang, *J. Nanosci. Nanotechnol.*, 2011, **11,** 1941.

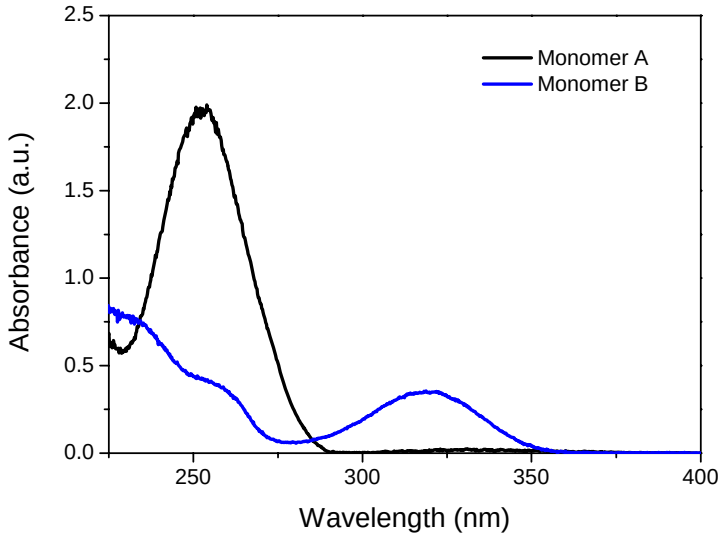
Supplementary Figures



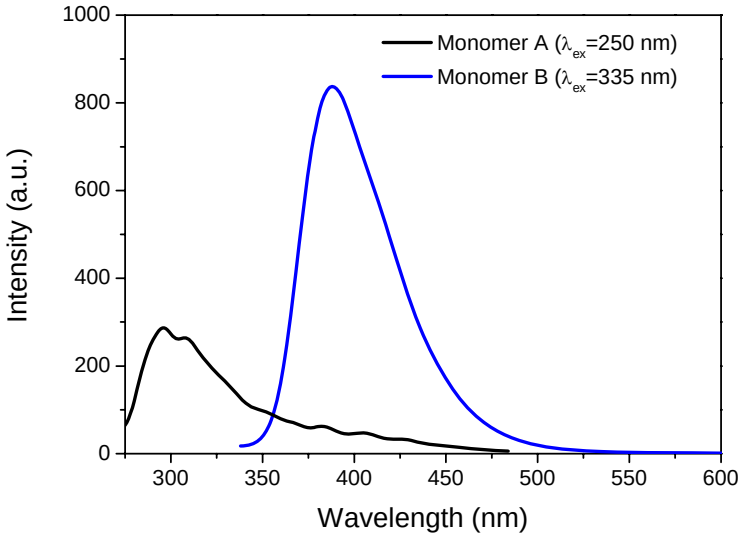
Monomer A: 4,4'-difluorobenzophenone



Monomer B: 3-trifluoromethyl hydroquinone

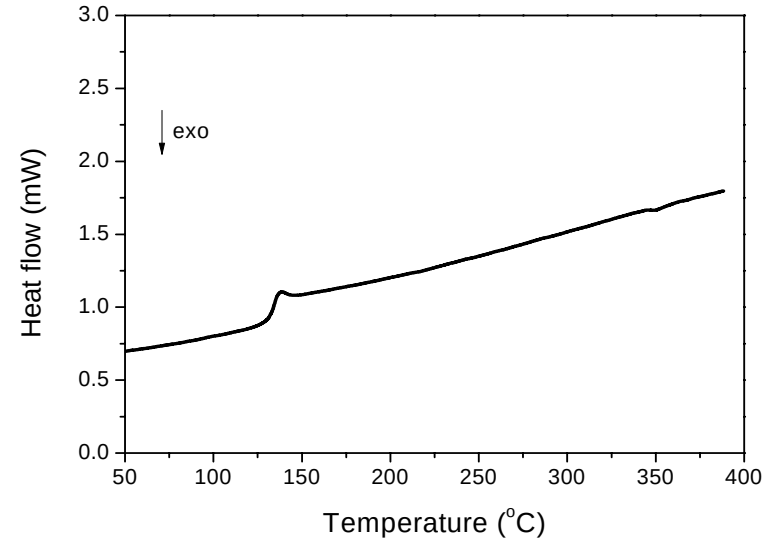


(a)

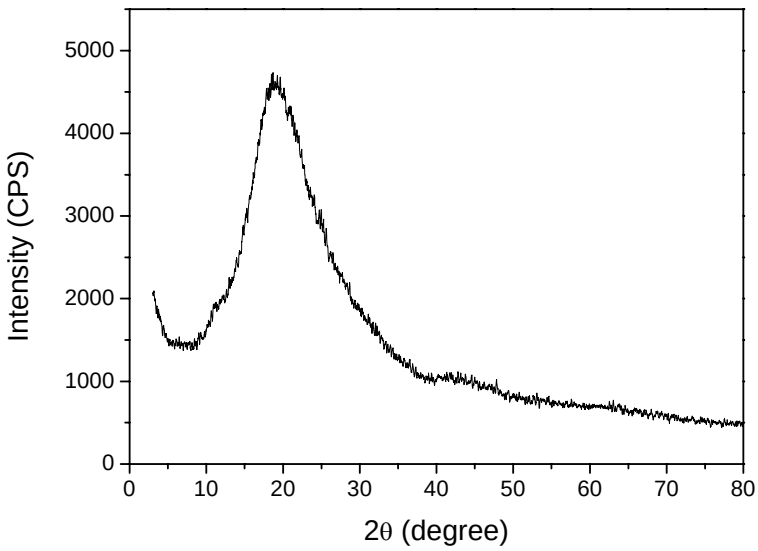


(b)

Figure S1. Fluorescence results of the monomers used for the synthesis of FPEEK. a: UV absorbance, b: fluorescence emission.



(a)



(b)

Figure S2. DSC and XRD curves of FPEEK film. Amorphous state of the FPEEK is confirmed.

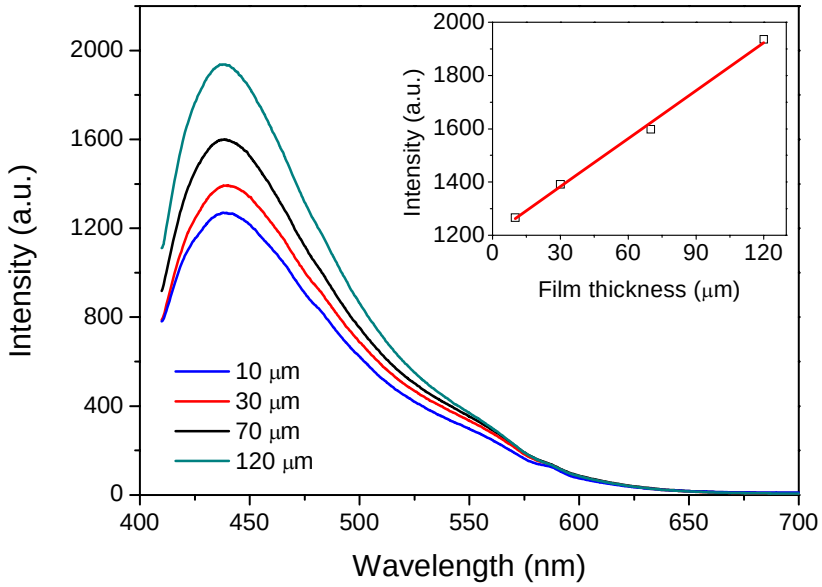
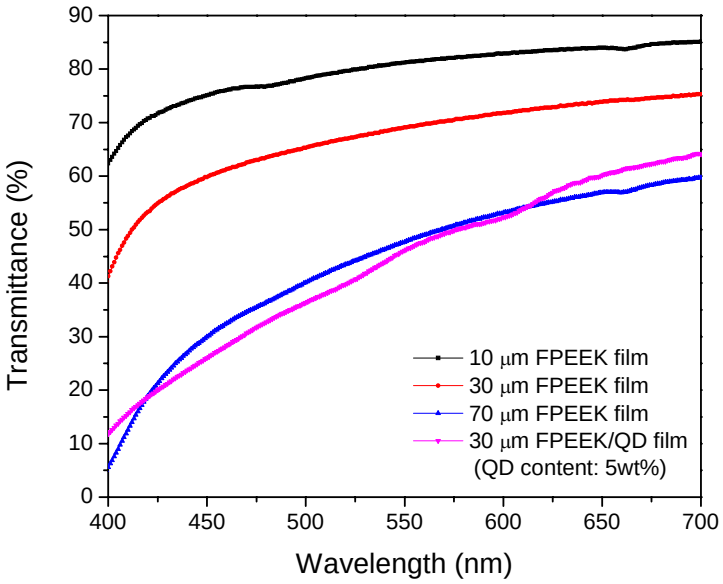
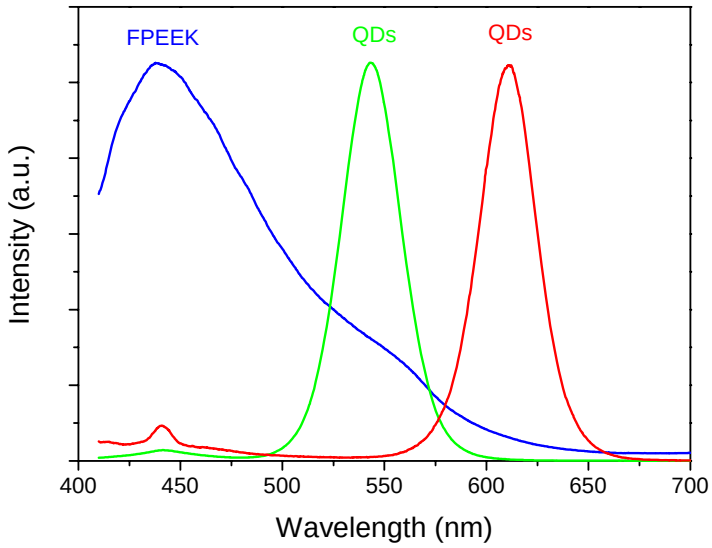


Figure S3. Fluorescence intensity of FPEEK film with different thicknesses. Inset: linear relationship of fluorescence intensity at 440 nm as a function of film thickness ($R^2 = 0.995$).

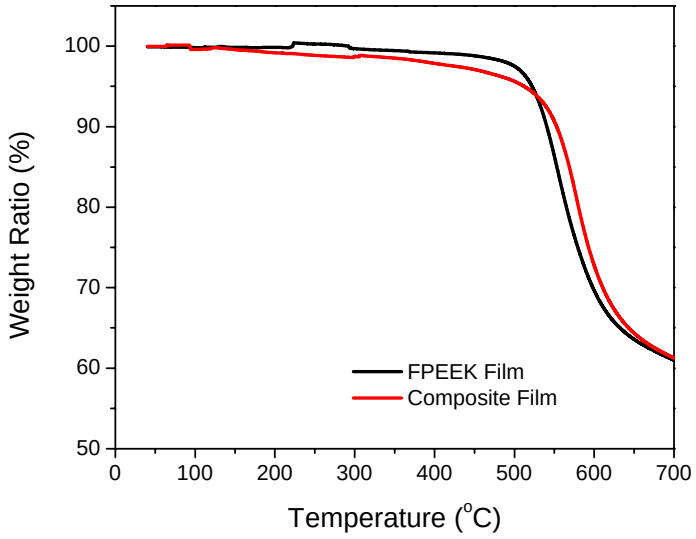


(a)

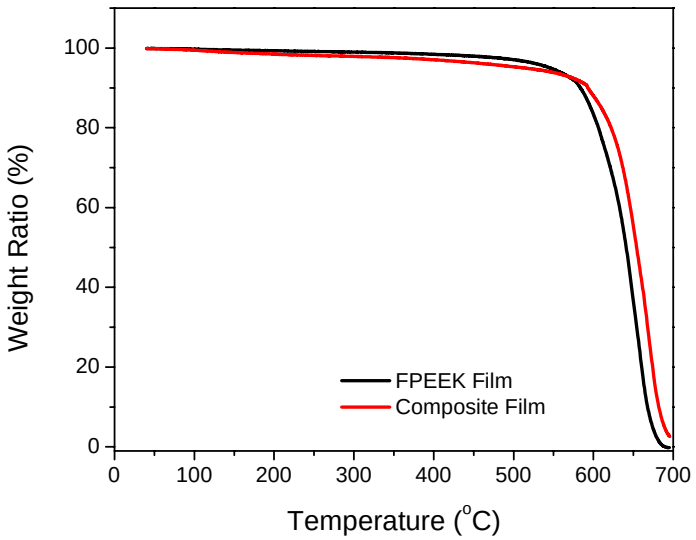


(b)

Figure S4. (a) Transmittance of FPEEK and FPEEK-QD composite films measured using UV spectrophotometer. (b) Fluorescence emission spectra of FPEEK film (blue curve) and n-hexane solution of the two kinds of QDs (green and red curves) used for manufacturing the FPEEK-QD composite films.

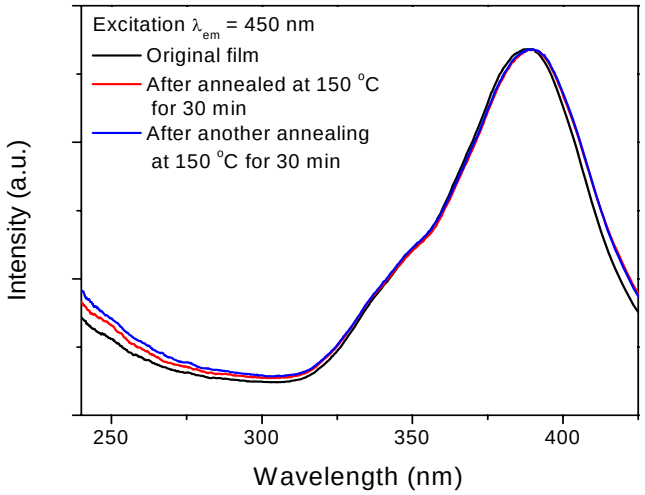


(a)

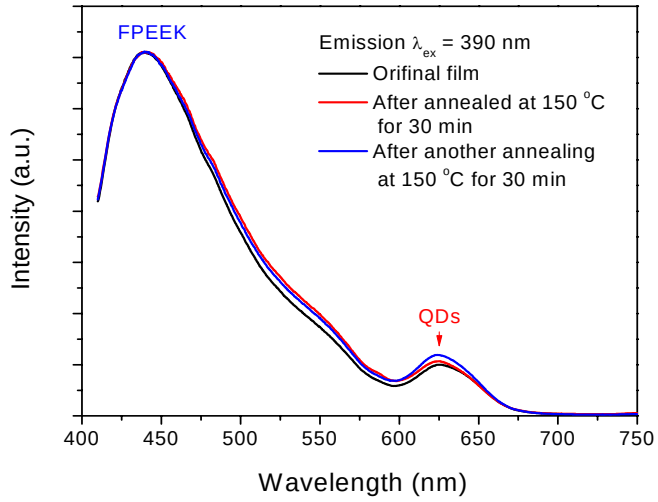


(b)

Figure S5. TGA diagrams of FPEEK film and FPEEK-QD composite film (containing 3wt% QDs) under nitrogen (a) and in air (b).



(a)



(a)

(b)

Figure S6. Demonstration of thermo-stability of a FPEEK-QD film (containing red-emitting QDs). (a) Fluorescence spectra. Up: excitation, down: emission. (b) Optical image of the FPEEK-QD film upon an annealing at 150°C for 30 min. Left: before annealing, Right: after annealing. For the annealed film, the fluorescence spectra and the photograph were taken after the film was cooled down to ambient temperature.