

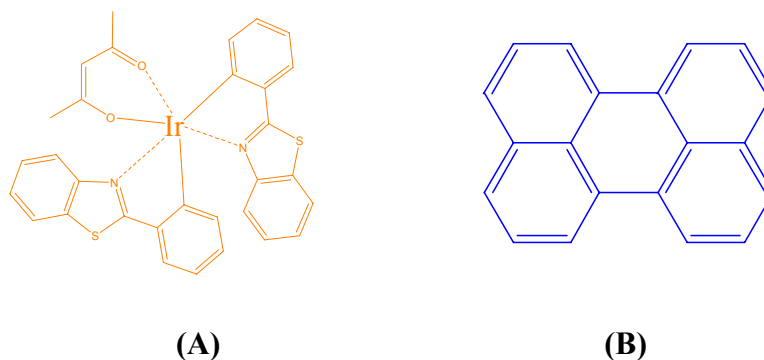
# **Organic Core-Shell Nanostructures: Microemulsion Synthesis and Upconverted Emission**

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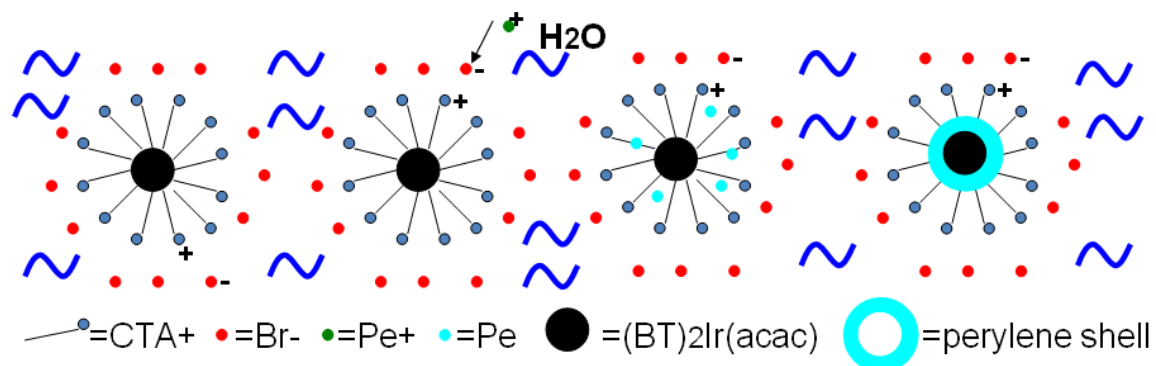
**Electronic Supplementary Information (ESI)**

### Experimental details

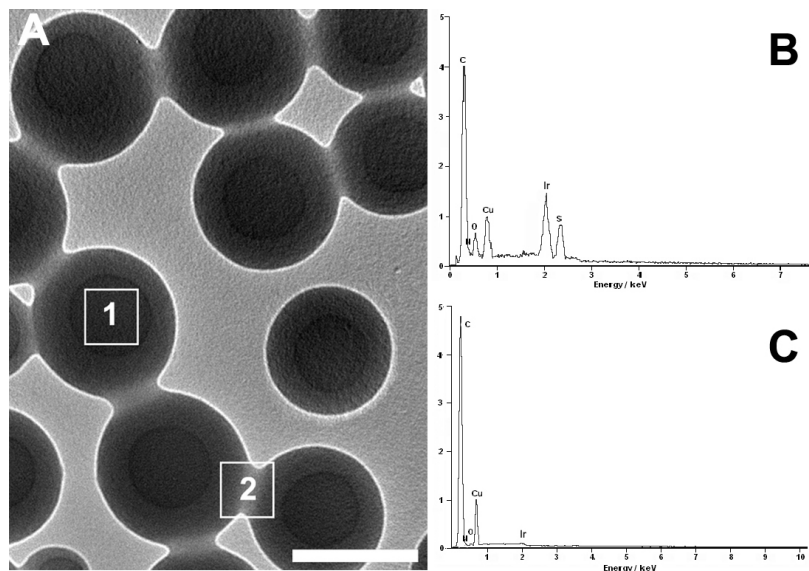
The  $(\text{BT})_2\text{Ir}(\text{acac})$  was synthesized according to the literatures [M. L. Xu, R. Zhou, G. Y. Wang, J. Y. Yu, *Inorg. Chim. Acta* 2009, **362**, 515-518; S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M. E. Thompson, *Inorg. Chem.* 2001, **40**, 1704-1711.] Perylene was purchased from Aldrich, and perylene perchlorate precursor was prepared with our previously reported method [L. Kang, Z. Wang, Z. Cao, Y. Ma, H. Fu, J. Yao, *J. Am. Chem. Soc.* 2007, **129**, 7305-7312.] The preparation of the  $(\text{BT})_2\text{Ir}(\text{acac})@$ perylene core-shell nanoparticles were described in detail in the text. The diameter of the  $(\text{BT})_2\text{Ir}(\text{acac})$  core was kept to be  $\sim 30$  nm by fixing the preparation conditions, while the thickness of the perylene shell is modulated by changing the adding amount of the perylene perchlorate precursor. The core-shell nanoparticles were transferred onto copper grids by drop cast for TEM measurements with a JEOL JEM-2010, and onto quartz wafers for measurements of PL spectra with a HITACHI F-4500 fluorescence spectrophotometer at an excitation of 500 nm, and PL images with an Olympus IX71 inverted microscope by exciting the samples with an Ar ion laser at 514.5 nm on an inverted microscope, and the emission signals were collected with an objective from the top and detected with a colored CCD. The excitation laser was filtered with a 514 nm notch filter. The power dependence of the upconverted emission was excited with an Ar ion laser at 514.5 nm and taken with a grating Andor Shamrock 303 spectrometer matched with a TE-cooled EMCCD Camera.



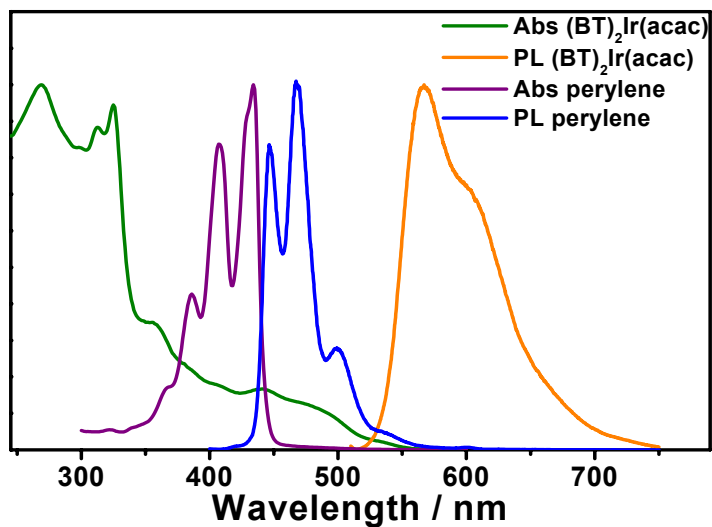
**Scheme 1** Molecular structures of  $(\text{BT})_2\text{Ir}(\text{acac})$  (A) and perylene (B).



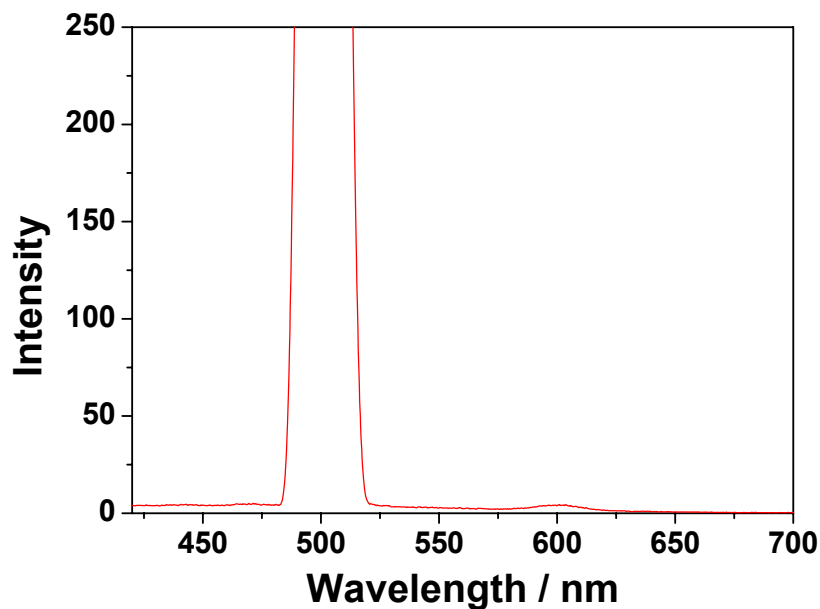
**Figure S1** Schematic illustration about the formation process of the perylene shells from perylene cations. CTA<sup>+</sup>Br<sup>-</sup> molecules were ionized in aqueous phase. The perylene cations were attracted by Br<sup>-</sup> and reacted with H<sub>2</sub>O to produce perylene molecules. Then the reduced perylene molecules nucleated into the CTAB micelles (*Adv. Mater.* 2003 **15**, 977), and encapsulated the (BT)<sub>2</sub>Ir(acac) cores due to their hydrophobic nature. As a result, a shell layer was formed outside the (BT)<sub>2</sub>Ir(acac) in the CTAB micelles.



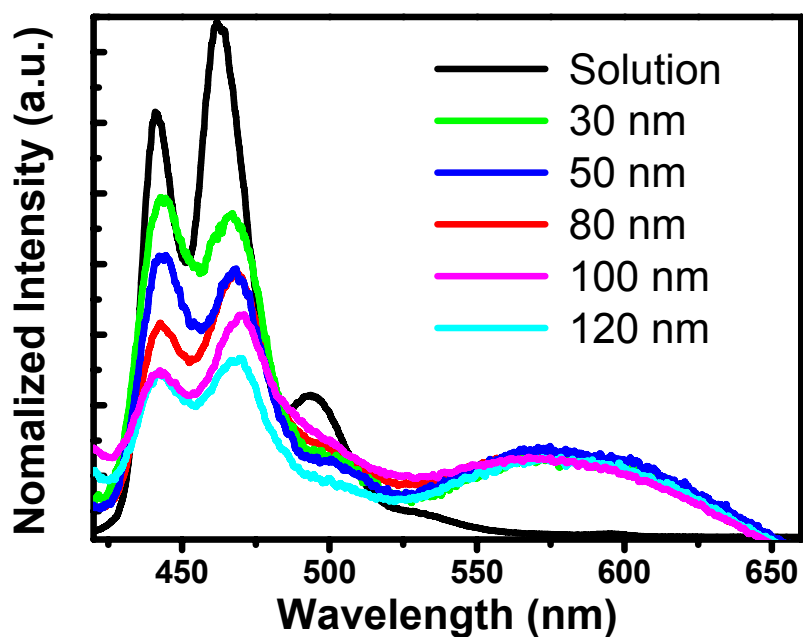
**Figure S2** EDX spectra of the  $(\text{BT})_2\text{Ir}(\text{acac})@\text{perylene}$  core-shell nanoparticles. (B) was taken from the area 1 in (A), and (C) from area 2. The Cu peak is from the TEM grid. There are intense peaks of Ir, S, and O in the core layer, while the shell layer is mainly C element. This proves that the composite nanoparticles are composed of  $(\text{BT})_2\text{Ir}(\text{acac})$  cores and perylene shells.



**Figure S3** Normalized absorption and photoluminescence spectra of (BT)<sub>2</sub>Ir(acac) and perylene monomers measured in acetonitrile and ethanol, respectively. Perylene was excited with 385 nm, while (BT)<sub>2</sub>Ir(acac) was excited with 500 nm and measured under air free condition.



**Figure S4** PL spectra (excited with 500 nm) of pure perylene nanoparticles prepared with reprecipitation method. The peak at 500 nm is from the excitation light. The result indicates that perylene itself is not luminescent under green excitation, and the blue PL band in the core-shell nanoparticles are from the triplet-triplet energy transfer between  $(\text{BT})_2\text{Ir}(\text{acac})$  and perylene, and the subsequent triplet-triplet annihilation based upconversion.



**Figure S5** PL spectra (excited with 385 nm) of pure perylene nanoparticles prepared with reprecipitation method. The results indicate that the diameters (30, 50, 80, 100, 120 nm, on average) of perylene nanoparticles determine the relative emission intensities of monomer and aggregates. When the pure perylene particle size is about 30 nm (green line), the monomer emission (420-500 nm) is much stronger than the aggregate emission (550-600 nm). The perylene shells (10-20 nm in thickness) in the core-shell nanostructures are properly expected to produce more monomer emission and less aggregate emission than the 30 nm pure perylene nanoparticles.