A facile route to bulk high-*Z* polymer composites for gamma ray scintillation†

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Two classes of bulk high-*Z* polymer composites were prepared, which exhibit scintillation properties for γ-radiation detection.

The detection of high energy γ rays is important to public health and security. Inorganic high-Z (Z = atomic number) compounds have been extensively studied for γ-ray detection.[1] However, the application of these semiconductors has serious drawbacks such as the need for ancillary cooling systems, modest stopping powers, high cost, radiation intolerance and poor energy resolution. For example, ZnCdTe can be operated at room temperature, but it is challenging to grow large-size perfect crystals.[2] NaI(Tl) scintillation is a good room temperature detector, but its energy resolution is limited.[3] Bulk germanium provides high energy resolution but requires operation at liquid nitrogen temperature.[4] It has been a significant challenge to develop γ-ray detectors with high sensitivity, good energy resolution, and low fabrication cost.

Conjugated polymers have been suggested as radiation detection materials based on either their electrical or optical properties.[5,6] Initially, conjugated polymers were studied mainly to detect radiation from charged particles, such as electrons,[5,7] protons,[8] and α particles.[9] The use of conjugated polymers for the detection of X- and γ-rays is still limited by several factors, the main being that they respond to the radiation only at very high dosages (>1 kGy).[10,11] Solvents of higher Z increase the polymer's sensitivity to radiation;[12] however, the measurement is based on the cumulative radiation effect, the total dosage of the X- or γ-ray exposure.[13] Many applications require real-time radiation detection. Scintillation spectrometry can be used for medical imaging, nuclear and particle physics, non-destructive evaluation, and environmental monitoring. Organic materials, such as naphthalene, anthracene, polymers, and doped polymers, have been studied as γ-ray scintillators, although the sensitivity has been limited by the low Z of these materials.[14–17]

A composite containing an inorganic high-Z compound and a polymer could exhibit γ-ray scintillation by the mechanism illustrated in Fig. 1.[7] The photophysics is different from that of the charge transfer passive mode for photoluminescence (PL) quenching detection.[18] The scintillation mode shown in Fig. 1C is based on fluorescence resonance energy transfer (FRET) from the high-Z component to the luminescent polymer in the composite material. Upon γ irradiation, the high energy photons are attenuated and absorbed by the high-Z compound, where electron–hole pairs are produced. The electron–hole pairs are subsequently transferred to the polymers, where they radiatively decay at high quantum efficiency. The emitted visible photons are then detected with a photomultiplier tube. This composite scintillator could possess high stopping power and fast decay time, both being essential for high energy resolution.

An ideal γ scintillation material is transparent with negligible scattering of the photons produced by the radiation scintillation. It also has high density and large effective Z to effectively attenuate γ photons. Therefore, to achieve a high-Z polymer composite for γ scintillation, poly(trimethylolpropane trimethylacrylate) (TMPTMA) was selected as the solid matrix. This polymer is colorless, transparent and compatible with a variety of organic and inorganic compounds.[19]

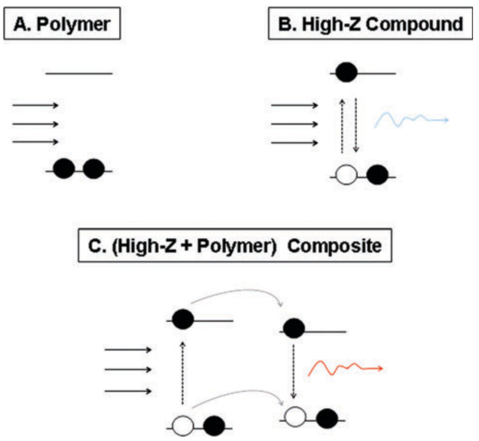

Fig. 1 Schematic illustration of the γ scintillation photophysics in a luminescent polymer (A), an inorganic high-Z compound (B), and their composite (C). Filled circles indicate electrons, and open circles holes. Horizontal straight arrows indicate γ radiation.

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† Electronic supplementary information (ESI) available: Structure of P-PPV; photographs of BiI_3–octylamine complex solutions and a composite containing 10 wt% BiI_3; excitation and photoluminescence spectra of the composite films; experimental setup for gamma scintillation measurement. See DOI: 10.1039/b813571a

Into the poly(TMPTMA) matrix was blended a luminescent conjugated polymer, P-PPV[20] (see ESI,† Scheme S1 for the chemical structure), and a high-Z compound at high weight ratios. An inorganic compound, BiI_3, was selected as the high-Z ingredient. BiI_3 can be dissolved in certain polymers and has been studied for radiation detection.[21] An organic high-Z material, 1,3-diiodobenzene (DIB), was also used, in place of BiI_3, for its solubility in polymer films at high concentrations.[13]

In the preparation of BiI_3-containing composites, 3 g BiI_3 was dissolved in 10 ml THF. Subsequently, 0.3 g octylamine was added into the BiI_3 solution. The color of the solution changed from yellow to red with the addition of the amine ligand. The solution was agitated for 30 min to ensure complete coordination of BiI_3 with the ligand. Then 10–50 mg of P-PPV was added into the BiI_3 complex solution. After the P-PPV was totally dissolved, 25 mg of benzoyl peroxide (BPO) was added. Various amounts of TMPTMA monomer were then added dropwise under agitation to afford a uniform solution. THF was then removed on a rotary vacuum pump. The residue was poured into a casting mold, which was subsequently placed in a high-vacuum oven. The oven temperature was raised gradually to 75 °C and kept at this temperature for 10 h. The decomposition of BPO initiated the polymerization of TMPTMA. The resulting poly(TMPTMA) composites were >1 cm thick. The composites were separated from the mold and cut into different sizes with flat facets. The surfaces of the bulk samples were polished with 400 and 1000 mesh sandpaper, and Al_2O_3 nanoparticles successively. The DIB-containing composites were prepared in a similar manner, except that no octylamine was added.

Fig. 2 shows photographs of the polished poly(TMPTMA) composites doped with 50 wt% DIB and 30 wt% BiI_3. The green and blueish green emission colors under UV irradiation are from P-PPV in the composites.

The vacuum environment was important for the achievement of clear bulk composites, especially for the BiI_3 doped composites. When the molds loaded with TMPTMA solutions were placed on a hotplate in air to initiate polymerization, instead of in a vacuum oven, BiI_3 in the solution precipitated gradually when the temperature was raised to 40 °C. The precipitation was observed even when the doping concentration of BiI_3 was only 10% (see ESI,† Fig. S1). The resulting composite was opaque (see ESI,† Fig. S2). In addition, the complete removal of residual THF in the solution before thermal curing was initiated was also important. Any residual THF would form bubbles and cracks in the resulting bulk composites.

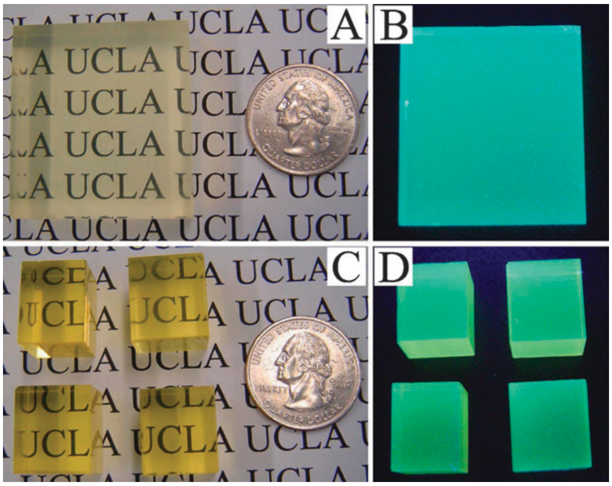

Fig. 2 Optical photographs of composites containing 50 wt% DIB (A, B) or 30 wt% BiI_3 (C, D), taken at bright field (A, C) or under UV radiation (B, D). A US quarter-dollar coin indicates the dimensions of the composite materials.

Fig. 3A shows the absorption spectra of BiI_3 composites with different weight percentages of BiI_3 and P-PPV. The composites exhibit two absorption bands at 400 nm and 425 nm. Comparison with the absorptions of the three components in their individual solutions indicates that the absorption of the composites in the 350–400 nm region is contributed by BiI_3, and the band in the 400–450 nm region should be attributed to P-PPV. The relative absorbance is affected by the amounts of both BiI_3 and P-PPV in the composites.

The density of the DIB composite was 1.32 g cm^{-3}, and that of the BiI_3 composite was 1.6 g cm^{-3}. The effective Z values of the composites were calculated using:[22]

$$Z_{\text{eff}} = \sqrt[2.94]{f_1 \times Z_1^{2.94} + f_2 \times Z_2^{2.94} + \cdots} \tag{1}$$

where f_n is the fraction of the total number of electrons of element n in the composite, and Z_n is the atomic number of element n. The effective Z of the DIB composite was calculated to be 33.8, while that of the BiI_3 composites was 42.7.

The excitation and photoluminescence spectra of the composites are shown in Fig. 3B. With the content of P-PPV kept at 0.1%, increasing the amount of BiI_3 from 20 wt% to 30 wt% enhances the PL intensity of P-PPV by 200%. This

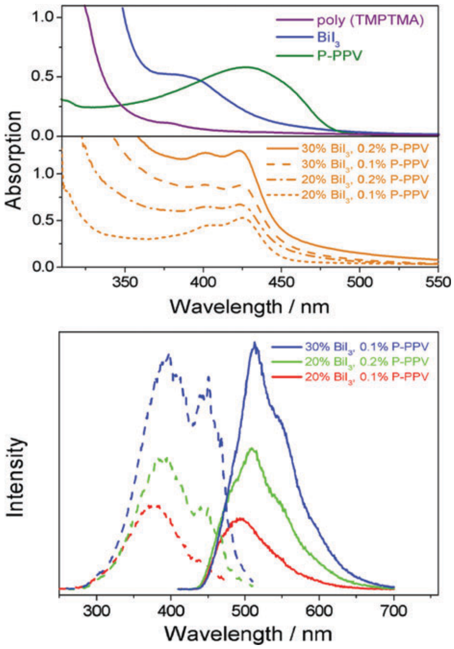

Fig. 3 (A) Absorption and (B) excitation (dotted lines)/emission (solid lines) spectra of BiI_3 composites with specified weight concentrations of BiI_3 and P-PPV. To enable comparison, the absorption spectra of solutions of pure BiI_3 and P-PPV and thin films of pure poly(TMPTMA) are shown in (A).

means that FRET energy transfer occurs from BiI_3 to P-PPV,[23] whereas charge transfer between BiI_3 and P-PPV is not significant. As a result, the P-PPV in the composites can be excited with the whole wavelength range from 300 nm to 500 nm. When the concentration of BiI_3 is fixed at 20 wt%, increasing the P-PPV content from 0.1 wt% to 0.2 wt% almost doubles the PL intensity. However, further increasing the concentration of P-PPV causes aggregation of P-PPV and PL quenching (see ESI,† Fig. S3). The intensity of the emission from the DIB composites is similar to that from BiI_3 composites when the weight concentration of P-PPV in the composites is 0.2% (see ESI,† Fig. S3). The emission peak is slightly blue shifted compared to that for the BiI_3 composite, which is consistent with the subtle difference in the luminescent images shown in Fig. 2. This blue shift can be caused by the partial degradation of P-PPV by iodine free radicals during the polymerization of TMPTMA.[18]

To investigate the scintillation properties of the as-prepared composites, the decay profiles and energy spectra were measured by coupling the samples to a Hamamatsu H8500 Photomultiplier Tube (see ESI,† Fig. S4 for the experimental setup). Analog signals were sent to a Digital Signal Processing unit for pulse processing. Event data were recorded in list mode format. Waveforms were digitized and captured using a 6 GHz oscilloscope. Exponential fit was used to calculate the $1/e$ decay constant (τ). Composite samples containing (A) 30 wt% BiI_3 and 0.5 wt% P-PPV, (B) 20 wt% BiI_3 and 0.5 wt% P-PPV, and (C) 50 wt% DIB and 0.5 wt% P-PPV were measured. All three composites revealed typical scintillation properties with lifetimes of 17, 15, and 16 ns, respectively. These are comparable to those of $LaCl_3$[24] and $LaBr_3$,[25] although the scintillation efficiencies of the composites are lower. Photocount measurements were obscured by the rather large background count rate suggesting energy trapping and a phosphorescence component of luminescence decay.

In conclusion, two classes of high Z polymer composites were prepared. By controlling the reaction conditions, transparent bulk composites were obtained with thickness of >1 cm, containing 30 wt% of BiI_3 or 50 wt% DIB. Fluorescence resonance energy transfer from BiI_3 to the luminescent polymer was observed under UV irradiation, indicating the feasibility of such composites for γ scintillation wherein the high-Z compound functions as the γ photosensitizer and the polymer as the energy acceptor to produce visible photons. The luminescence of the composites is stable enough to ensure repeated measurements. The scintillation properties are expected to be further improved by increasing the contents of high Z compounds.

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