Designer colors for radiation detection

Mark Allendorf, F. Patrick Doty, and Patrick L. Feng

Novel radiation detection concepts are generated by doping both conventional and nanoporous scintillators with triplet-harvesting molecules.

Radiation detection is vital for preventing the illicit movement of radiological and nuclear materials around the globe, as well as for space exploration, nuclear power, and other critical applications in the chemical, biological, and medical fields. Current radiation detection methods that rely on liquid scintillation are limited in terms of speed and sensitivity, which are crucial elements for dynamic detection scenarios such as at border crossings. In these applications, reducing detector interference from naturally occurring radiation—that could come from anything from bananas to medical isotopes—would reduce false-alarm rates and increase sample throughput.

Discrimination of fast neutrons from background gamma rays is typically accomplished using organic scintillators that are capable of pulse-shape discrimination (PSD). These organic scintillators can, when excited by a high-energy particle, emit light from the first excited singlet state (S1; see Figure 1). Particle types with different linear energy transfer (LET) can be distinguished from one another by differences in the time-dependent scintillation light, which is composed of a fast component from S1 and a long-tailed delayed distribution from annihilation of two triplet (T1) excitons. The intensities of useful delayed light and detrimental power-law afterglow depend on the lifetime and mobility of the T1 states, which is difficult to control and is easily disrupted by disorder or a variety of nonradiative trapping processes. Unfortunately, rational design of new PSD scintillators is very difficult because performance-limiting phenomena, such as pulse pileup and afterglow, are controlled by complex mechanisms that govern the triplet annihilation kinetics.

Our new approach to particle detection is enabled by doping organic scintillators with organometallic complexes to create hybrid materials that emit light of various colors when they interact with high-energy particles. Known as spectral-shape discrimination (SSD), this method enables neutrons to be distinguished from ubiquitous background gamma rays based on the ratio of emitted light at two different wavelengths. We recently discovered that infiltrating the nanopores of scintillating metal-organic frameworks (MOFs) with so-called ‘triplet harvester’ molecules produces a differential response to ionizing radiation based on particle type. MOFs are a diverse class of supramolecular crystalline materials with pores or channels that do not collapse upon removal of guest molecules. An example of a scintillating MOF is DUT-6, shown in Figure 2. The combination of inorganic metal ions and organic ‘linker’ groups that compose their structure enables them to be tailored for a wide range of nuclear detection applications.

Figure 1. Diagram of the energy levels and energy transport processes in an organic scintillator, such as a metal-organic framework (MOF) doped with triplet-harvesting molecules. S0: Ground state. S1: Singlet state. T1: Triplet state. PSD: Pulse shape discrimination. MLCT: Metal-to-ligand charge-transfer.
By lightly doping the MOF nanopores with transition-metal complexes containing heavy elements such as iridium, we created a two-state system in which exponential luminescence associated with triplet excitons is generated by fast energy transfer from the MOF triplet to the dopant (see Figure 1), which then efficiently emits in the visible region of the spectrum. Since triplet excitons constitute ~75% of the excited states formed by ionizing particles, the quantum yield of MOF scintillators can be increased as much as fourfold over traditional scintillators, such as organic crystals and polymers. A related concept is used to increase quantum yields in organic light-emitting diodes.6,7

Since this initial discovery, we determined that doping certain plastics allows SSD as well,8 which is important for applications such as wide-area detectors for portal monitoring, for which economical scintillators are needed. As shown in Figure 3, light produced by the triplet harvester acetylacetonato-bis(2-phenylpyridine)iridium—abbreviated as Ir(ppy)$_2$(acac)—at 515nm is well separated from the emission from singlet excitons emitted by the polymer polyvinylcarbazole (PVK) host at 420nm. The ratio of the intensities at these two wavelengths depends on the identity of the particle, leading to SSD and enabling an alternative to PSD for particle discrimination. The low doping level also implies a high triplet mobility in these materials, since on average the complexes are spatially separated by ~13nm.

A critical aspect of material design for SSD is dopant concentration, which must be controlled so that both the scavenged triplet light and fluorescence from the excited host (polymer or MOF) are emitted. Using typical triplet-harvesting molecules, such as tris-phenylpyridine iridium, we find that dopant levels as low as 200ppm iridium (weight/weight) are sufficient for effective SSD to occur (see Figure 4). This equates to about one complex molecule for every 50 pore cages in a scintillating MOF such as DUT-6. The upper doping limit is ~1% by weight; above this concentration, conversion of host luminescence to dopant emission becomes significant.

These new scintillation materials and SSD detection have several additional advantages for nuclear detection applications. First, active interrogation schemes, which use pulsed radiation sources to create a signal from fissionable nuclear material, are feasible since afterglow is reduced compared with conventional PSD materials. This may also permit the threshold for detecting fission neutrons to be reduced using SSD; current detectors are often overwhelmed by the high level of background gamma particles. Second, these materials can be tuned to maximize timing performance at high particle-detection rates. Third, they are solid, non-single-crystal, bulk scintillators that are nontoxic and nonflammable compared with many liquid organic scintillators used for PSD.
Figure 4. Unnormalized cathodoluminescence spectra for PVK samples doped with 0.025%, 0.05%, and 0.20% by weight Ir(ppy)$_2$(acac). The additive effect of guest luminescence is indicated by the black arrow for higher dopant concentrations.

Finally, SSD as a detection method is appealing because detecting two colors of light is relatively straightforward and should be inexpensive to implement. As a result, doped MOF and plastics scintillators represent new platforms for rational scintillator design, enabling completely new kinds of detection methods to be envisioned using materials tailored to particular detection needs. Currently, we are seeking industry partners to test these materials in realistic detection scenarios and scale up their production for commercialization.

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Author Information

Mark Allendorf, F. Patrick Doty and Patrick L. Feng
Sandia National Laboratories
Livermore, CA

Mark Allendorf is a senior scientist in the Center for Biological and Materials Sciences. His research is focused on fundamental and applied aspects of nanoporous materials, including applications in radiation and chemical sensing, electronic devices, and energy storage.

Patrick Doty is a distinguished member of the technical staff in the Radiation and Nuclear Detection Materials and Analysis Department. His research interests concern the development of materials and devices for radiation detection, including both organic and inorganic semiconductors and scintillators.

Patrick Feng is a senior member of the technical staff in the Radiation and Nuclear Detection Materials and Analysis Department. His research interests concern the development of novel materials for radiation detection.

References