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Tunable Two-color Luminescence and Host–guest Energy Transfer of Fluorescent Chromophores Encapsulated in Metal-Organic Frameworks

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Co-assembly of chromophore guests with host matrices can afford materials which have photofunctionalities different from those of individual components. Compared with clay and zeolite materials, the use of metal–organic frameworks (MOFs) as a host structure for fabricating luminescent host–guest materials is still at an early stage. Herein, we report the incorporation of a laser dye, 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM), into stilbene-based and naphthalene-based MOF systems. The resulting materials exhibit blue/red two-color emission, and the intensity ratio of blue to red fluorescence varies in different planes within the MOF crystal as detected by 3D confocal fluorescence microscopy. The observed changes in ratiometric fluorescence suggest the occurrence of energy transfer from MOF host to DCM molecules, which can be further confirmed by periodic density functional theoretical (DFT) calculations. Moreover, selective changes in luminescence behavior are observed on treating the guest@MOF samples with volatile organic compounds (methanol, acetone and toluene), indicating that these host–guest systems have potential applications as fluorescence sensors. It can be expected that by rational selection of MOF hosts and guest chromophores with suitable emissive colors and energy levels, a wide variety of multi-color luminescent and energy-transfer systems can readily be prepared in a similar manner.

The incorporation of fluorescent guest molecules into the nanochannels of host matrices has attracted much recent attention in terms of both fundamental studies and the development of applications in light emitting diodes[1], polarized emission[2], lasers[3], and other optoelectronic devices[4]. As a result of host–guest interactions and collective effects, the resulting organized assemblies can also display unique functionalities (such as emission properties and photo-/thermal-stabilization) which are not simply the sum of those of the individual components[5]. Metal–organic frameworks (MOFs), also known as coordination polymers, are a class of regular crystalline solids with intrinsically well-organized host structures formed by the coordination of metal cations/clusters with organic units[6–9]. Recently, functional MOFs have been shown to have potential applications in many areas including gas storage/separation[10,11], catalysis[12,13], non-linear optics[14], and magnetism[15,16]. In addition, organic ligand-based luminescent MOFs have also been developed as fluorescence sensors during the last decade[17–28]. To date, compared with other host frameworks (such as one-dimensional (1D) nanotubes[29], two-dimensional (2D) layered clays[30] and three-dimensional (3D) zeolite materials[31]), the study of the encapsulation of guest chromophores into 3D MOFs is still in its infancy and examples are limited[32–34]. Therefore, how to rationally design suitable host porous topologies and select the guest species remains a major goal[35]. In addition, by introduction of chromophores with different emission properties into the MOF crystals, it should be possible to construct two-color luminescent systems for ratiometric fluorescence applications[36].

4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM, Figure 1A) is a well-known laser dye, which has attracted considerable attention as a red-color emissive material due to its high photoluminescent quantum yield and excellent optical and electronic properties[37]. In this work, we chose DCM as the fluorescent guest, and stilbene-based and naphthalene-based MOFs (stilbene-MOF[38] and naphthalene-MOF (also known as IRMOF-8[39]), Figure 1B and 1C) as the host matrices. Both stilbene-MOF and naphthalene-