Abstract

The concept of “aggregation-induced emission” (AIE) effect has induced a great deal of attention these days. Now, exploration of new AIE-active molecular system and multiple high technique applications for AIE materials are the two research hotspots. Cyanostilbene, as a classical structural unit in photoelectric functional materials, also exhibited this unique luminescence behavior. The research background was illustrated in Chapter 1, which mainly introduced the development of this subject. In this project, Chapter 2 and Chapter 3 presented two classes of functionalized AIE-active molecules based on cyanostilbene moiety, and their applications were investigated, while Chapter 4 demonstrated a series of donor-acceptor (D-A) molecules with highly emissive unit, and their photophysical properties were studied.

In Chapter 2, four different donor-substituted cyanostilbene-based dipyrrins were synthesized and characterized. The investigation of photophysical properties confirms that these molecules are AIE-active, which should be attributed to the cyanostilbene moiety. The introduction of different donor groups showed little impact on their luminescence. Furthermore, the emission properties of these molecules were found to be sensitive to Zn\(^{2+}\), that is, addition of Zn\(^{2+}\) enormously enhanced its fluorescence in THF. The titration experiments proved they showed good selectivity and sensitivity for Zn\(^{2+}\) detection with relatively low limit of
detection. Job’s curve and spectral studies of their corresponding zinc complex indicated that the ratio for dipyrrins and $\text{Zn}^{2+}$ is 2:1, which suggested the formation of zinc complex by chelation-enhanced fluorescence (CHEF) effect should be the reason of the enhanced fluorescence. By combining dipyrrin with typical AIE-active moiety tetraphenylethylene (TPE), an AIE-active TPE-based dipyrrin was prepared. The studies of its fluorogenic $\text{Zn}^{2+}$ detection confirmed that the CHEF effect together with AIE effect are responsible for the intense fluorescence, indicating the potential application as a $\text{Zn}^{2+}$ detector in aqueous media.

In Chapter 3, the cyanostilbene backbone was functionalized with a terpyridine unit to construct four terpyridine-based cyanostilbene molecules with different donor substitutents. The investigation of their photophysical properties confirms that they are AIEE-active. With the effect of different electron-donating groups, their solid-state fluorescence color was adjusted from blue to orange-red successfully. According to the calculation results of their frontier molecular orbitals, terpyridine has little impacts on their luminescence, but would influence their solid-state emission obviously owing to its large steric hindrance. This class of molecules displayed higher luminescence efficiency in solid state than in their dissolved state. The twisted molecular conformation in single crystal, which effectively avoids close $\pi-\pi$ stacking, was assumed to be responsible for the high luminescence efficiency in solid state. This kind of molecules show distinct
switched fluorescence by stimuli of acid/base vapors, and this phenomenon derives from the protonation effect of nitrogen atoms in the terpyridine unit. Moreover, three of these molecules exhibit good electroluminescence properties. Especially, the crystal of non-donor substituted molecule show amplified spontaneous emission (ASE) properties, indicating this blue-emissive material can be used in multiple areas such as chemical sensor, organic light emitting diodes (OLEDs) and organic laser media.

In Chapter 4, two highly emissive units (triphenylimidazole and phenanthroimidazole) were introduced to the D-A combination constructed by different donor groups and cyanostilbene moiety. The investigation of the photophysical properties suggested that all the molecules were AIEE-active. The introduction of imidazole induces another charge transfer (CT) state between imidazole and cyanostilbene groups. Quantum theory calculations for their frontier orbitals indicated hybridized local and charge transfer (HLCT) state with high luminescent efficiency may dominate the radiative process for all the molecules and the solvatochromic experiments with consistent PL spectral changes further confirmed the strong CT state in their emission process, which are mainly originated from the D-A structure. Furthermore, the imidazole-based donor-substituted cyanostilbene derivatives with high efficiency and thermal stability were thought to be potential emitters in the prospective applications of OLEDs. The two corresponding symmetric imidazole-containing
cyanostilbene-based molecules were prepared, which emit yellow fluorescence in the solid state owing to the extended conjugation length relative to their asymmetric ones. The triphenylimidazole-containing molecule showed a quicker growth rate than the phenanthroimidazole-containing one, indicating that more rotators make the molecule more AIE-active, and proved again, that the restricted intramolecular rotation (RIR) process is the main cause for the AIE phenomenon. The electronic cloud distribution from their calculated frontier orbitals indicated they are D-A-D structure with the side imidazole units as donor groups and the middle cyanostilbene as the acceptor part. The solvent effect of them demonstrated there was a charge transfer transition between imidazole and cyanostilbene in their excited state. Furthermore, both of the two molecules show good electroluminescence properties.
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