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Efficient piezochromic luminescence from tetraphenylethene functionalized pyridine-azole derivatives exhibiting aggregation-induced emission

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ABSTRACT

In this work, three tetraphenylethene-functionalized pyridine-azole derivatives were successfully synthesized and characterized. Their photophysical properties in both solution and solid-state were investigated systematically. All luminogens are almost non-emissive in solution but highly emissive in the aggregated states, showing aggregated-induced emission. Importantly, their crystalline aggregates exhibit effective piezochromism with high contrast in both emission color and intensity. The emission color between blue and green can be reversibly and quickly switched by a grinding-heating process several times without any deterioration. The experimental data clearly demonstrate that the interconversion between crystalline and amorphous states is response for the present piezochromism. Non-doped electroluminescence devices using the dyes as light-emitting layers were fabricated. The devices display a peak current efficiency of 2.3 cd A^{-1} and power efficiency of 2.0 lm W^{-1}, respectively. The obtained results will be useful in designing new efficient multifunctional materials and enriching piezochromic luminescent systems as well.

1. Introduction

Study of efficient solid state luminophors has attracted increasing interest on account of their various applications in the fields of optoelectronic devices, sensors and biomedical imaging [1–7]. It is well known that the emissions of the luminophors in the condensed phase strongly depend on the molecular arrangement motif and intramolecular interactions [8–11]. Thus, tuneable and switchable solid-state luminescence can be realized by application of an external stimulus that triggers the alteration of self-assembled structures [12–16]. Recently, great efforts have been devoted to molecular design of piezochromic luminescent (PCL) materials, which show dynamically switchable solid-state emissions in respect to the convenient mechanical stimulus such as grinding and shearing [17–23]. The easily controlled and reversible luminescent features of such materials make them promising candidates for applications in optical storage, sensors and security inks [24–27]. For the application in the real-world, it also requires that the PCL materials possess good reversibility, fast response and high contrast features. However, the controllable design and synthesis of such excellent materials still remains a great challenge. In addition, most conventional luminogens often suffer from the aggregation-induced quenching (AIQ) phenomena in the solid state, which make it difficult to achieve efficient PCL materials. Therefore, further development of new PCL materials with efficient emission and outstanding piezochromic features in the solid-state is extremely desirable.

In 2001, the group of Tang observed a unique luminescent phenomenon, aggregation-induced emission (AIE), which is precisely opposite to the AIQ effect: these AIE luminogens are almost non-emissive in solution but show strong luminescence when aggregated as nanoparticles or powders [28,29]. This finding provides a new strategy to construct efficient luminescent materials. Since then, a large number of AIE-active dyes have been developed and their potential applications have been evaluated [30–32]. Thus, to construct the PCL materials with efficient solid-state emission, it

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would be nice if the synthesized PCL materials can show AIE feature. However, limited examples of AIE-active PCL materials have been reported to date.

Recently, Huang and our group have developed a series of phosphorescent Ir(III) complexes exhibiting interesting piezochromism, in which the 2-(2-pyridyl)-benzimidazole (PyBM) and pyridinetriazole (PTA) moieties are used as ancillary ligands [33,34]. The photoluminescent color of Ir(III)-based phosphors can be altered by gentle grinding and recovered upon heating. The employed PyBM and PTA units have high electron affinities and high photoluminescence quantum yields (Φ_{PL}); these features have led to their extensive applications in optical devices [35,36]. Besides that, they are easily synthesized and decorated by the grafting of functional groups, endowing them with new functional properties. To our best knowledge, however, the pyridine-azole-based organic luminophors exhibiting PCL properties have yet to be reported. It is speculated that whether the pyridine-azole-based PCL dyes can be constructed by the ingenious molecular modification, which will develop new PCL systems to study and can also perform further molecular design to optimize the material characteristics.

According to previous studies, introduction of multiple adjustable interactions to organic dyes may produce polymorphism due to the varied balance of the weak interactions between molecules [37,38] Furthermore, if the resulting dyes exhibit twisted conformations, then loose packing patterns in the solid state will be observed, which can further facilitate the construction of the PCL materials [21,38–41]. From the structure point of view, if PyBM and PTA can be functionalized by bulky and twisted aromatic groups, then multiple weak interactions will form between the functional groups and its parent molecule, such as C–H … π and C–H … N interactions. These interactions can help to effectively enhance their solid-state emission because of the restriction of intramolecular rotations and afford the adjustable interactions as well as the loose molecular packing. As a result, the pyridine-azole-based PCL dyes will be constructed. To design and synthesize such materials, the first question is to resolve their AIQ effect. Herein tetraphenylethen (TPE) was chosen as the functional group due to its facile synthesis, splendid AIE effect and inherent twisted molecular conformations [42]. Keeping this in mind, we have designed and synthesized three pyridine-azole-based materials modified by TPE unit, i.e. FPTA-TPE (**C1**), PTA-TPE (**C2**) and PyBM-TPE (**C3**) (see Scheme 1). Their photophysical properties in both solution and solid-state were investigated in detail. As expected, three luminogens **C1**, **C2** and **C3** show not only AIE properties but also intriguing PCL characteristics. Gratifyingly, a reproducible two-color emission writing/erasing process for such materials can be achieved successfully *via* grinding and heating. With the merit of their AIE characteristics, non-doped multilayer organic light-emitting diodes (OLEDs) using them as emitting-layers have been fabricated, which shows a peak current efficiency up to 2.3 cd A^{-1} and powder efficiency of 2.0 lm W^{-1}, respectively.

2. Experimental section

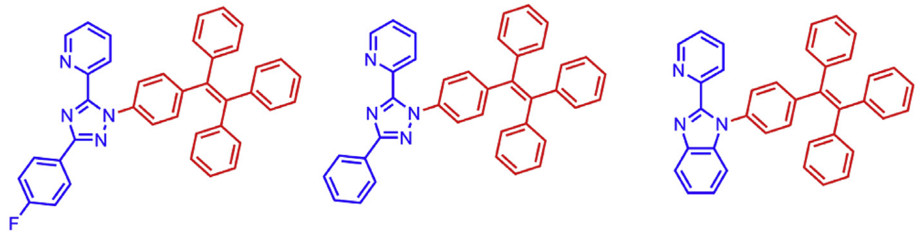
2.1. Materials and instruments

All materials and solvents were commercially available and used as received without further purification. All manipulations were performed under a dry nitrogen atmosphere using standard techniques. Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer TG-7 analyzer under nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) curves were obtained with a Perkin–Elmer thermal analysis DSC-7 under nitrogen with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku-Dmax 2000. ^{1}H NMR spectra were recorded using a Bruker AV 500 MHz with tetramethylsilane (TMS) as the internal standard. The molecular masses were determined using electrospray-ionization. The high-resolution mass spectral (HRMS) analysis was performed using Bruker Daltonics flex Analysis. Emission spectra were recorded using the F-7000 FL spectrophotometer. Emission spectra were measured at their maximal excitation wavelengths. Absolute photoluminescence quantum yields were determined using an integrating sphere system.

2.2. Synthesis

2.2.1. Synthesis of compound C1

A mixture of intermediate 2-(3-(4-fluorophenyl)-1*H*-1,2,4-triazol-5-yl)pyridine (1.44 g, 6.0 mmol), (2-(4-bromophenyl) ethene-1,1,2-triyl)tribenzene (2.71 g, 6.6 mmol), copper(I) iodide (0.11 g, 0.60 mmol), 18-crown-6 (16 mg, 0.06 mmol), K_2CO_3 (1.2 g, 9.0 mmol) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, 5 mL) was heated to 190 °C for 24 h under a N_2 atmosphere. After cooling to room temperature (RT), the reaction was quenched with 2 N hydrochloric acid and then the reaction mixture was extracted with CH_2Cl_2. After washing with aqueous NH_3 and water, drying over anhydrous Na_2SO_4, and evaporating the solvent, the residue was purified by column chromatography on silica gel (ethyl acetate: petroleum ether = 1:2) to give the desired product as a white powder. Yield: 64%. T_m: 247 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.51 (d, J = 5.0 Hz, 1H), 8.20–8.23 (m, 2H), 7.81 (d, J = 7.5 Hz, 1H), 7.74–7.78 (m, 1H), 7.30–7.33 (m, 1H), 7.06–7.26 (m, 17H), 7.02–7.05 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 164.62, 162.64, 160.95, 153.27, 149.37, 147.29, 144.36, 143.37, 143.25, 143.03, 141.91, 139.71, 136.60, 136.52, 131.86, 131.37, 131.33, 131.19, 128.56, 128.49, 127.77, 127.73, 127.67, 126.69, 126.65, 124.67, 124.31, 124.28, 115.59, 115.42. IR (cm^{-1}): v = 3415 (m), 3073 (w), 3019 (w), 1736 (w), 1598 (m), 1510 (s), 1490 (m), 1467 (s), 1417 (s), 1269 (w), 1225 (m), 1154 (m), 1001 (s), 843 (s), 753 (s), 699 (s), 641 (m). HRMS (m/z), found: $[M + H]^+$ 571.2286; molecular formula $C_{39}H_{27}FN_4$, requires $[M + H]^+$ 571.2220.



C1 **C2** **C3**

Scheme 1. Chemical structures of **C1**, **C2** and **C3**.