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Switching the emission of tetrakis(4-methoxyphenyl)ethylene among three colors in the solid state†

Chenyu Li,[a] Xiaoliang Luo,[a] Weijun Zhao,[a] Cuihong Li,[a] Zhengping Liu,[a] Zhishan Bo,[a] Yuping Dong,[b] Yong Qiang Dong*[a] and Ben Zhong Tang*[cd]

Emission of a luminogen could be switched among three colors in the solid state by transformation among three different aggregation states. The partly amorphous solid of the luminogen exhibits excitation dependent emission due to the contribution of both amorphous and crystalline parts to the photoluminescence intensity.

Considerable effort has been devoted to the development of stimuli-responsive luminescent materials due to their fundamental importance and potential applications in sensors,[1] memory[2] and security inks.[3] Of particular interest are those luminogens whose emission can be switched between different colors or between dark and bright states in the solid state through modulating their molecular packing pattern.[4]

The emission of some luminogens can be modulated reversibly by repeatedly tuning luminogen aggregates between amorphous and crystalline[5] or between two different crystalline states[6] through solvent fuming, heating or mechanical stress. However, emissions of many luminescent materials can be switched between only two luminescent states as the materials can merely form two emissive states. Though several luminogens do emit multicolor lights in various states, reversible luminescence switching among multiple colors has rarely been achieved. Emission of a liquid crystal mixture has been reported to be tuned reversibly among reddish-orange, yellow, and green.[7] Jia and co-workers have also achieved multicolor emission switching of two luminogen-functionalized peptides through modulation of molecular packing patterns and mechanochemical reaction.[8] Furthermore, there is still no clear design strategy for such materials.

Emissions of many panel-like organic luminescent materials are weakened or even quenched at high concentrations or in aggregate states, which is notoriously known as aggregation-caused quenching (ACQ).[9] We observed a phenomenon of aggregation-induced emission (AIE) which is the exact opposite of the ACQ effect: a group of propeller-shaped molecules are nonemissive in solution, but are induced to emit intensively by aggregate formation due to restriction of the rotation of their aryl rings.[4c,10] Some AIE active compounds exhibit increased PL intensity and blue-shifted emission when transforming from amorphous to crystalline states, which has been coined crystallization induced emission enhancement (CIEE).[11] Thus emission of those CIEE luminogens could be switched between two different colors through modulating their molecular packing pattern.

In this letter, we attached methoxyl groups to the *p*-positions of phenyl rings in the TPE molecule. Through introducing weak interactions (C–H$\cdots$O and C–H$\cdots\pi$) in the AIE molecule we obtained a luminogen exhibiting morphology dependent emission. The luminescence of the compound could be switched among three colors in the solid state through vapor, thermal and mechanical stimuli.

Luminogen **1** is nearly nonemissive in solution. However, when a large amount of water was added to the solution, **1** emitted strong green light with a peak at 491 nm due to the formation of aggregates in acetonitrile–water mixture (Fig. S1, ESI†). Thus, similar to other derivatives of TPE, luminogen **1** is AIE active.[10b]

Crystals of **1** were obtained by slow evaporation of its acetone solution and its molecular packing pattern is shown in Fig. S2 (ESI†). The crystal (**1CA**) emits deep-blue light with

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[a] Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing, 100875, China. E-mail: dongyq@bnu.edu.cn; Tel: +86-10-5880-6896

[b] College of Materials Science and Engineering, Beijing Institute of Technology, Beijing, 100081, China

[c] Department of Chemistry, The Hong Kong University of Science & Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong, China. E-mail: tangbenz@ust.hk

[d] Institute of Biomedical Macromolecules, MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China

† Electronic supplementary information (ESI) available: Experimental procedures, crystal structure of **1** (CIF), UV and PL spectra for **1**, DSC thermograms and powder XRD patterns of **1** in different aggregation states. CCDC 918901. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj00063j

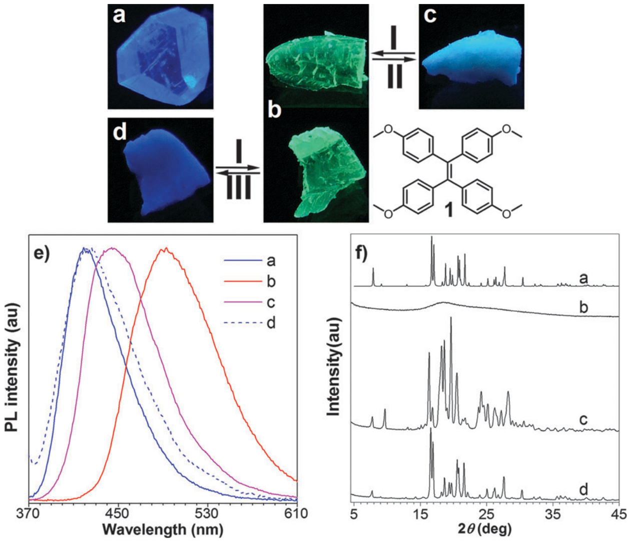

Fig. 1 Photos of (a) **1CA**, (b) **1Am**, (c) **1CB**, and (d) **1Am** fumed with acetone. (e) PL spectra (excitation wavelength: 338 nm), and (f) powder XRD patterns of samples (a–d) in the images. Photos were taken under UV illumination. I, Heating to melt and quickly cooling; II, 110 °C for 10 min; III, fuming with acetone vapour, 5 min.

a peak at 421 nm upon excitation. As many AIE luminogens have been reported to exhibit morphology dependent luminescence, we prepared the pure amorphous solid of **1** (**1Am**, Fig. 1b) through quenching its melt. **1Am** emits green light with a peak at 491 nm, which is about 70 nm red-shifted compared with that of **1CA**. When we tried to fume **1Am** with acetone vapor, **1CA** was obtained again. Thus the emission of luminogen **1** can be switched reversibly between green light (**1Am**) and deep-blue light (**1CA**) through repeated heating and solvent fuming.

Amorphous solids will crystallize upon heating before melting, thus we annealed **1Am** at 110 °C; however, **1Am** did not reform **1CA** upon heating but afforded another crystal (**1CB**) of luminogen **1**, which emits blue light with a peak at 442 nm. The powder X-ray diffraction (XRD) pattern of **1CB** also reveals that **1CB** is a new crystalline phase which is different from **1CA**. The exothermic peak at 82 °C in the differential scanning calorimetry (DSC) thermogram of **1Am** (Fig. S3, ESI†) indicated this cold crystallization process (from **1Am** to **1CB**). The DSC thermograms suggest that **1CA** and **1CB** melt at similar temperatures. **1CB** could be transformed to green emissive **1Am** again by quenching its melt. Thus the luminescence of **1** can also be tuned reversibly between green (**1Am**) and blue (**1CB**) through pure thermal methods. It is a pity that direct transformation between **1CA** and **1CB** cannot be achieved, though we have tried heating and solvent fuming, while both crystals can be transformed to **1Am** first and then to **1CA** through solvent fuming or to **1CB** through heating. Thus, it is clear that emission of **1** can be tuned reversibly among three colors.

Why does luminogen **1** exhibit morphology dependent emission? The propeller-like conformation of molecule of **1** rules out any specific strong intermolecular interactions (such as π–π stacking or H/J-aggregates) between molecules, thus, the emission of luminogen may depend on the conformations of its molecules. The varied equilibria of the weak interactions (such as C–H···O and C–H···π, Fig. S2, ESI†) between molecules in the solid state may afford different balanced conformations, hence the morphology dependent emission. It is impractical to obtain conformation information on molecules in amorphous or crystalline powder form, thus details of the molecular conformations of **1CB** and **1Am** are not accessible. Fortunately, the single crystal structures of tetrakis(4-propoxyphenyl)ethylene (TPPE, CCDC 865201) and tetrakis(4-butoxyphenyl)ethylene (TBPE, CCDC 865202) with PL spectra peaking at 448 and 446 nm respectively,[12] have been reported. The methoxy, propoxy and butoxy groups display similar inductive effects on the photophysical properties of the TPE core. Thus different emissions from the three TPE cored luminogens should be caused by their varied conformations. As we expected, the average value of the torsion angles of the phenyl rings in **1CA** (55°) is larger than those for TPPE (47°) and TBPE (46°).[12] The larger torsion angle induces lower conjugation, which coincides with the bluer emission of **1CA** than those of TPPE and TBPE. Thus the morphology dependent emissions of such propeller-shaped molecules may be due to the various conformations in different aggregates.

The weak interaction between molecules in the loosely packed aggregates of **1** could be readily broken and rebuilt, hence facilitating its transformation between different aggregate states and emission switching.

Mechanochromic luminescent materials have received considerable attention due to their potential applications in mechanical sensors and optical storage.[12,13] Deep blue emissive **1CA** transforms to green emissive powder (Fig. 2b under 365 nm UV light) upon grinding in a mortar. However, when excited with 254 nm light from a UV lamp, the ground powder emits blue light. In addition to the visual observations, we studied the excitation dependent emission of **1** using a PL spectrofluorometer. The PL spectra also blue-shifted from 490 nm to 446 nm when the excitation light changed from 399 to 300 nm. Thus the emission of the ground solid can be switched between blue and green just through changing the excitation light between 254 nm and 365 nm. What is the cause of the mechanochromic and excitation-dependent fluorescence of luminogen **1**?

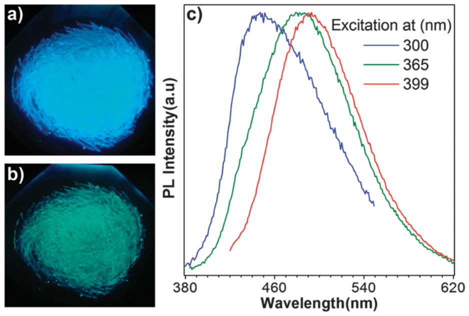

Fig. 2 (a, b) Photos of ground solid obtained on grinding **1CA** in a mortar taken under a (a) 254 nm and (b) 365 nm UV lamp. (c) Excitation dependent PL spectra of the ground solid.

Organic crystals can be transformed into an amorphous powder upon grinding. Powder XRD and DSC of the ground and annealed powder from **1CA** were measured to disclose the mechanism of mechanochromic fluorescence. The diffraction pattern of the ground solid exhibits some reflections that agree with those of **1CA** and the annealed crystal but does not have as many or as sharp peaks, hinting at a not absolutely amorphous phase. The diffraction curve of the annealed sample displays many sharp and intense reflection peaks that coincide with those of **1CA**, indicating their same crystalline order. The exothermic peak at 59 °C in the DSC thermogram of the ground solid (Fig. S4b, ESI†) indicates the phase transformation from the amorphous to the crystalline phase. Thus the mechanochromic fluorescence of **1** is caused by the amorphization of crystals upon grinding and the emission reverts back to deep-blue upon heating.

None of the pristine crystal, amorphous solid and annealed ground solid of **1** exhibit excitation dependent emission (Fig. S5, ESI†). Why does the ground solid behave differently? As grinding a large amount of sample in a mortar affords a not absolutely amorphous solid, thus the emission of the ground solid may originate from both amorphous solid and pristine crystals. The excitation spectra (Fig. S6, ESI†) of pristine crystals and amorphous solid revealed that when excited with light below 344 nm, both crystals and amorphous solid contribute to the PL spectra. When the excitation wavelength is larger than 344 nm the contribution of pristine crystals to the PL intensity drops quickly, and no PL signal is observed when the excitation wavelength is larger than 390 nm. On the other hand, as the excitation increases from 270 to 400 nm, the PL intensity (490 nm) of the amorphous solid increases, thus contributing more to the PL spectrum. It is clear that the decreased contribution from the crystals and the increased contribution from the amorphous solid of luminogen **1** with excitation increase induced the excitation dependent PL spectra of ground solid of **1**.

As it is difficult to obtain absolutely amorphous solid through grinding a large amount of sample in a mortar, thus we sheared a tip of a crystal of **1** with a spatula on the inner wall of a quartz cell. The PL spectrum of the ground powder was independent of excitation and fit well with that of the amorphous solid of **1**, (Fig. S7, ESI†) indicating its amorphous essence. The emission of the ground powder reverted back to deep-blue when heated, which was different from that of the amorphous solid of **1**. Though the PL spectrum of the ground solid fit well with that of **1Am**, trace amounts of tiny crystals of **1** in the ground solid may serve as nuclei to afford **1CA** on heating. Fuming with solvent vapor also transformed the ground solid to the original deep blue crystals, which coincided with **1Am**. Thus the emission of **1** could be switched reversibly between green and deep-blue through repeated grinding and heating or repeated grinding and fuming processes (Fig. 3).

If we start from **1CB**, the emission of ground solid could be turned to deep-blue through fuming with solvent vapor, or to blue through heating (Fig. S8, ESI†).

The mechanochromic fluorescence of **1** prompted us to study its potential application as an optical recording material. **1CA** was ground on one piece of weighing paper, and we obtained a piece of green emissive paper (Fig. 4). Then the emission of the paper turned from green to deep blue, in accordance with the **1Am** to **1CA** phase transition. Next we wrote the Chinese word for teacher on the paper, and then a green Chinese word appeared on the deep blue background due to the amorphization of **1CA** in the written area. The green word was erased upon heating due to the transformation of **1** in the word area from amorphous to crystal. Then we could repeat the writing and erasing process many times through repeated shearing and heating processes. Thus luminogen **1** may find application in optical recording due to the high sensitivity and low background noise of luminescence-based materials.

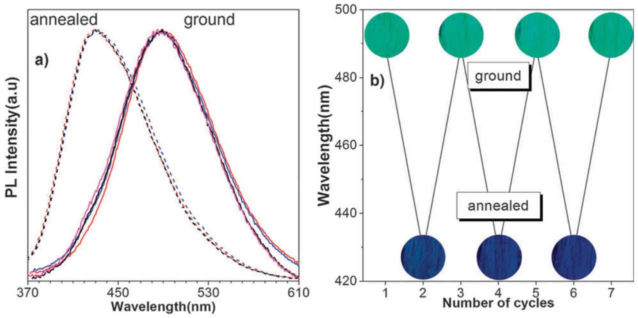

Fig. 3 Normalized (a) PL spectra of ground and annealed solid of **1** in the three repeat cycles. Annealing conditions: 110 °C, 1 min. (b) Switching the fluorescence of luminogen **1** by repeated shearing on the inner wall of a quartz cell and heating.

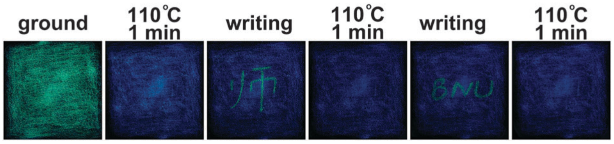

Fig. 4 Procedure of repeated writing and erasing process using luminogen **1** as an emissive material. Photoluminescent images were taken on a piece of weighing paper under UV irradiation at 365 nm.

In conclusion, a luminogen exhibiting multicolor emission switching was obtained through introduction of weak interactions to an AIE active molecule. The partly amorphous ground solid from **1CA** exhibits excitation dependent emission. The varied equilibria of the weak interactions afford morphology dependent emission of the luminogen, and the loose packing pattern endued by the propeller-like conformation of the AIE active molecules facilitates transformation among different aggregate states. Hence we provide a possible design strategy for emission switching materials.

Experimental

1 was synthesized by a typical self-McMurry coupling reaction. A 250 mL two-necked flask equipped with a magnetic stirrer was charged with zinc dust (3.3 g, 50 mmol) and 60 mL THF under a nitrogen atmosphere. The mixture was cooled to 0 °C, and $TiCl_4$ (2.75 mL, 25 mmol) was added slowly by syringe. The mixture was refluxed for 2.5 h and cooled to 0 °C. The raw material 4,4′-dimethoxybenzophenone (4.8 g, 20 mmol) in THF (60 mL) was added to the mixture. Then the mixture was refluxed until TLC showed complete conversion. The reaction was quenched with saturated aqueous NH_4Cl solution, and extracted with diethyl ether. The organic layer was desiccated with anhydrous magnesium sulfate for 2 h, and then filtered. The solvents were removed by evaporation. Finally the resulting residue was purified by recrystallization from acetone to give a white powder **1** (3.5 g, 75%). M.p. 181–182 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 3.67 (s, 12H, OCH_3), 6.67–6.69 (d, 8H, Ar-H), 6.84–6.86 (d, 8H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 157.38, 137.94, 136.18, 131.88, 113.11, 54.81. IR: 2832, 1604, 1509, 1455, 1296, 1239, 1167, 1032, 832. HRMS (ESI) calculated for $C_{30}H_{28}O_4$ $[M+H]^+$: 453.2060; found, 453.2073.

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