DOI: 10.1002/anie.201204660

Photoluminescence

Piezochromic Luminescence Based on the Molecular Aggregation of 9,10-Bis((*E*)-2-(pyrid-2-yl)vinyl)anthracene**

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Luminescent materials sensitive to environmental stimuli are of great interest from a scientific viewpoint owing to their potential applications in fluorescent switches and optical devices.[1] Pressure is one of the most common natural external stimuli, and thus piezochromic materials, which show color changes resulting from external pressure or mechanical grinding, can be used as pressure-sensing and optical-recording systems. However, whereas pH-, light-, and temperature-sensitive materials are relatively well understood, studies of piezochromic materials remain inadequate owing to the absence of an effective mechanism to explain the relationship between changes in molecular assembly or packing and the corresponding luminescence properties of the material. Until now, successful systems have generally made use of transformations between monomeric and dimeric/excimeric states through hydrogen-bonding interactions as the mechanism to cause changes in luminescence.[2] It is well-known that in the condensed phase, the luminescence properties of a given molecular system usually undergo significant variation according to the molecular aggregation state or stacking mode, since intermolecular interactions invariably alter photophysical processes.[2c,3] Therefore, an understanding of and the ability to control the molecular aggregation state and the consequent intermolecular interactions are still very important for the development of piezochromic materials.

Herein we report an effective mechanism of piezochromic luminescence on the basis of the molecular aggregation state of 9,10-bis((*E*)-2-(pyrid-2-yl)vinyl)anthracene (BP2VA). BP2VA exhibited spectacular luminescence characteristics: grinding and the exertion of external pressure on the powder led to a change in its photoluminescence color from green to red. Three crystal polymorphs of BP2VA with different stacking modes involving gradually enhanced π–π interactions in the three crystalline states provided further insight into the origin of luminescence changes under the external stimulae.

BP2VA was synthesized in a straightforward manner by a one-step Witting–Horner reaction according to a previously reported method,[4] and the purified material was characterized by spectroscopic methods (see the Supporting Information).

BP2VA powder exhibited a strong green emission at $\lambda_{max} = 528$ nm, in contrast to its weak orange emission at $\lambda_{max} = 583$ nm as a solution in THF. The weak orange emission was ascribed to a conformational relaxation in solution, which was reflected by the corresponding photoluminescence (PL) spectrum of BP2VA at low temperature (77 K; see Figure S1 in the Supporting Information).[5] Furthermore, the emission of BP2VA aggregation as a solution in THF/water was blue-shifted to $\lambda_{max} = 570$ nm (from the value $\lambda_{max} = 583$ nm in THF; see Figure S2). Interestingly, after being ground, BP2VA powder showed a strong red shift with a yellow emission ($\lambda_{max} = 561$ nm) under UV light with a wavelength of 365 nm, and after being heated above 160 °C, the ground powder recovered its initial green emission ($\lambda_{max} = 528$ nm; Figure 1 b,c). The interconversion of the two states with their distinct emission colors is completely reversible through grinding and heating. The red shift of 33 nm in fluorescence emission upon grinding and the recovery of the initial state upon heating is a significant piezochromic effect.

To gain further understanding of the piezochromic effect, we investigated the influence of applied pressure on the luminescence of BP2VA. The powder was placed in the holes (diameter: 200 μm) of a T301 steel gasket, which was preindented to a thickness of 50 μm. A small ruby chip was inserted into the sample compartment for in situ pressure calibration according to the R1 ruby fluorescence method. A 4:1 mixture of methanol and ethanol was used as a pressure-transmitting medium (PTM). The hydrostatic pressure on the powder was determined by monitoring the widths and separation of the R1 and R2 lines. The photoluminescence measurements under high pressure were performed on a QuantaMaster 40 spectrometer in the reflection mode. The 405 nm line of a violet diode laser with a spot size of 20 μm and a power of 100 mW was used as the excitation source. The diamond anvil cell (DAC) containing the sample was put on a Nikon fluorescence microscope to focus the laser on the sample. The emission spectra were recorded with a monochromator equipped with a photomultiplier. All experiments were conducted at room temperature.[6]

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[**] This research was supported by the 973 program (2009CB623605), the NSFC (Grant No. 20874035, 21074045, 21073071), and the Project of Jilin Province (Grant No.20100704).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201204660.

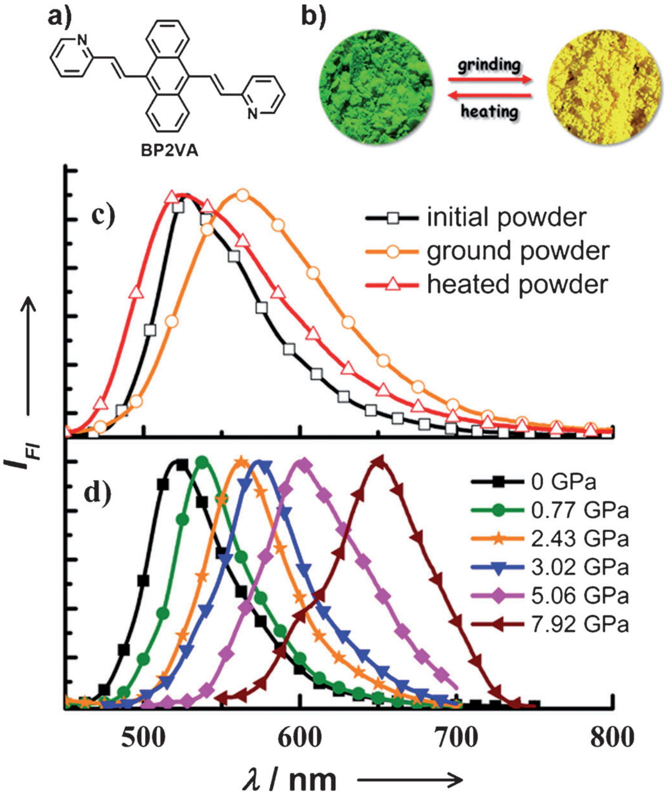

Figure 1. a) Molecular structure of BP2VA. b) Photographs of the ground powder and the heated powder under UV light (365 nm). c) PL spectra of the initial, ground, and heated powders. d) PL spectrum of BP2VA powder under external pressure. I_F = fluorescence intensity.

As the applied pressure increased, the fluorescence emission of the BP2VA powder clearly showed a gradual red shift (Figure 1 d). Applied pressure from 0 to 8 GPa caused a more noticeable color change in the luminescence of the BP2VA powder than was observed upon grinding. The observed color change from green (528 nm) to red (652 nm) is the largest piezochromic shift reported to date.[7] The PL spectrum with $\lambda_{max} = 561$ nm under an applied pressure of 2.43 GPa was quite similar to that of the powder ground with a pestle. An increased applied pressure of 7.92 GPa caused the luminescence to change to a redder emission with $\lambda_{max} = 652$ nm; apparently the grinding method is not powerful enough to cause a stronger piezochromic effect in the case of BP2VA. We believed that the dramatic change in the color of luminescence of BP2VA powder under applied pressure was the result of changes in the molecular aggregation state under external pressure.

Single crystals with a highly ordered molecular packing structure can be used to determine the relationship between the molecular aggregation state and luminescence properties directly and definitively. By the slow diffusion of ethanol or petroleum ether vapor into a solution of BP2VA in chloroform, single crystals with three polymorphs (C1, C2, and C3) suitable for X-ray structural analysis were obtained. Through systematic analysis of the three crystal polymorphs, we found that their stacking structures were completely different.[8] All BP2VA crystal polymorphs belong to the monoclinic system, and the molecular columns formed show a herringbone arrangement (see Figure S3). In the case of C1, molecules adopt a stacking mode of J-type aggregation along the *y* axis, whereas in C2, H-type aggregation occurs along the *x* axis. In particular, dimers in a tight face-to-face stack are found in C3 along the *x* axis. The overlap of anthracene planes between the adjacent molecules is increased from C1 to C3. The different stacking modes in C1, C2, and C3 reasonably result in different molecular aggregation states and thus lead to different fluorescence colors. These results clearly indicate that BP2VA forms three or even more different aggregation structures in the solid state. Furthermore, from C1 to C3, the three crystals showed a red shift in their absorption and emission, and a decrease in the fluorescence quantum yield (C1: 0.48, C2: 0.37, C3: 0.28).

In terms of the contribution of the frontier orbitals of the BP2VA molecule, the anthracene core is mainly responsible for the intramolecular radiative HOMO→LUMO transition (see Figure S4). Consequently, the stacking mode and intermolecular interaction of the anthracene planes should influence the HOMO–LUMO band gap as well as the luminescence of the molecular crystalline state. The anthracene planes of two adjacent molecules in C1 hardly overlapped at all (Figure 2 a), so there was nearly no π–π interaction in C1, which therefore exhibited green emission with $\lambda_{max} = 527$ nm. As for C2, the adjacent anthracene planes overlapped with each other by about 40 %, and the vertical

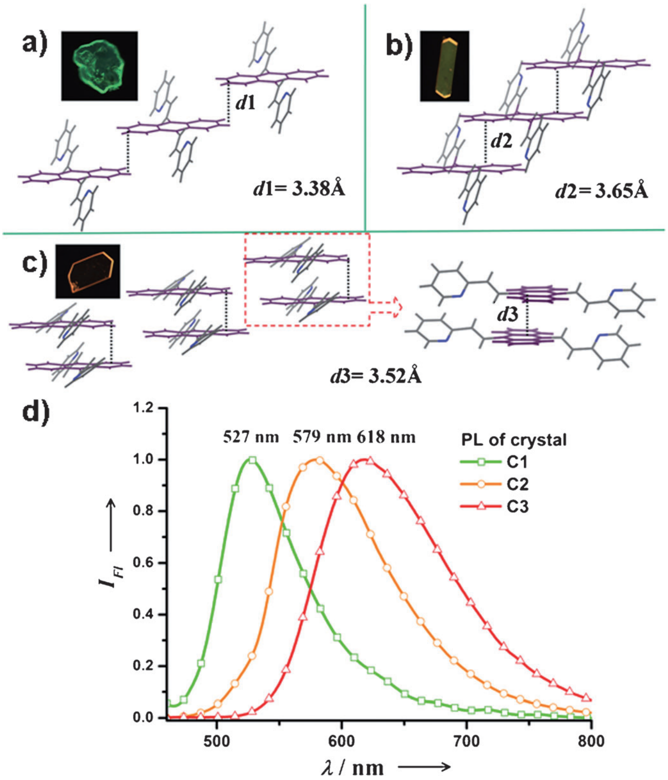

Figure 2. Stacking modes of the anthracene planes in adjacent BP2VA molecules in three single crystals: a) C1, b) C2, and c) C3. d) PL spectra of the three crystals.

distance between them was measured to be approximately 3.65 Å, which corresponds to the formation of weak π–π interaction between the anthracene planes (Figure 2 b). Thus, C2 was an orange-emissive crystal ($\lambda_{max} = 579$ nm). In the case of C3, molecules were bound together by a strong π–π interaction to form pairs in which the adjacent anthracene planes overlapped almost in a face-to-face stack with a distance between them of approximately 3.52 Å (Figure 2 c). This strong π–π interaction induced the red emission of C3 with $\lambda_{max} = 618$ nm. The red shift of the emission relative to those of C1 and C2 can be ascribed to the smaller band gap of the BP2VA molecule in C3 owing to the increased band widths of both the HOMO- and the LUMO-derived band as a result of the increased π–π interaction, according to a tight-binding model.[9] Nonetheless, another important factor for the red-shifted fluorescence should be taken into consideration, that is, the increase in exciton coupling and orbital overlap between neighboring molecules from C1 to C2 to C3. Increased exciton coupling and orbital overlap could lead to a strong red shift of the emission of the lowest state of the coupled chromophores.[3c] This enhanced intermolecular coupling is consistent with the increased density of the three crystal polymorphs (see Table S1 in the Supporting Information). Therefore, the PL emission of BP2VA in the aggregate/solid state could be changed by altering its molecular stacking mode.[10]

To gain more insight into the origin of the piezochromic properties of BP2VA powder, we studied the phase characteristics of the BP2VA powder by powder X-ray diffraction (PXRD) analysis (see Figure S5), with simulated patterns from the single-crystal data as a reference. The PXRD pattern of unground BP2VA powder agreed well with the simulated XRD pattern obtained from the crystal data of C1. It suggested that the initial samples adopt the same molecular arrangement as that of the C1 polymorph, with J-type aggregation along the molecular long axis and no effective π–π interaction between the central anthracene planes. Although some resolvable peaks of the ground sample were consistent with those of the unground sample, the intensity was weaker, which indicates that the initial aggregation state was changed by grinding. The orange emission of ground powder with $\lambda_{max} = 561$ nm was similar to the emission of C2 ($\lambda_{max} = 579$ nm), which showed red-shifted fluorescence and a blue-shifted absorption relative to the fluorescence and absorption of the unground powder (see Figure S6). These results suggested that H-type aggregation similar to the molecular packing of C2 possibly occurred during the grinding process,[11] although some of the initial aggregation state remained after grinding. The red shift observed upon grinding of the powder possibly originated from enhanced exciton coupling between the pairs of neighboring chromophores; exciton coupling already occurred over a long distance in the unground powder, despite the very small orbital overlap. This explanation is supported by the blue shift observed from the emission of the unground powder to that of BP2VA in solution at 77 K, under which conditions the molecule is completely in a single-molecular state.[12]

As mentioned above, the PL spectrum of BP2VA powder under external pressure underwent a larger red shift of approximately 125 nm from 528 nm at 0 GPa to 652 nm at 8 GPa. The range of this shift totally covered the corresponding spectra of the three crystals C1 (527 nm), C2 (579 nm), and C3 (618 nm). The density of the three crystal polymorphs increased from C1 to C3, and increasing pressure would be expected to shift the equilibrium to the densest form. Thus, the application of a higher pressure may lead to a material with a much greater density than that of the C3 polymorph. The piezochromic luminescence observed indicated that when pressure was applied, BP2VA powder underwent a transformation between the molecular aggregation states of the three crystals (Figure 3). In this process, external pressure impelled the molecular aggregation state of BP2VA powder to transform from J-type aggregation, such as that of C1, to H-type aggregation, as found for C2, and further to aggregated dimers stacked in a more tightly bound face-to-face arrangement, as in the case of C3. Meanwhile, the intermolecular π–π interaction strengthened gradually and thus induced the PL spectrum of the powder to change from a green emission (no π–π interaction) to an orange emission (weak π–π interaction) and then to a red emission (strong π–π interaction). Therefore, the ability of the molecular aggregation state to change upon grinding or under pressure leads to the changeable fluorescence color and the piezochromic effect in BP2VA powder.

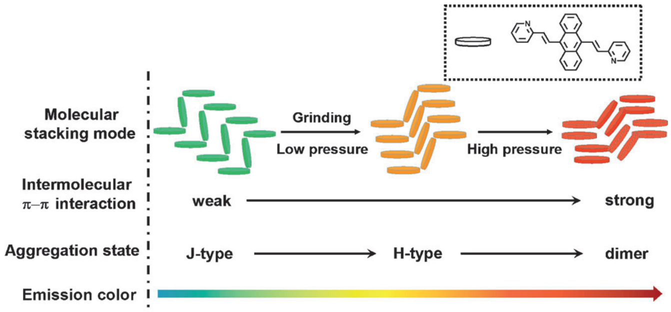

Figure 3. Stacking modes and corresponding emission colors for the various molecular aggregation states in BP2VA powder.

In conclusion, we have discovered a novel example of piezochromic luminescence in the molecule BP2VA, which exhibits distinctly different fluorescence emission in its three crystals. On the basis of single-crystal structural, photophysical, and computational studies, we found that enhanced π–π interaction between adjacent anthracene planes in the crystal and increased exciton coupling and orbital overlap between neighboring molecules induced the shift in fluorescence emission from green to red. The PL spectra showed that changes in the molecular aggregation state in BP2VA powder upon grinding or under external pressure led to an enhanced intermolecular π–π interaction and thus induced the piezochromic luminescence. This color-switchable feature of BP2VA may have potential for application in optical-recording and temperature- or pressure-sensing materials.

Received: June 14, 2012
Revised: August 29, 2012

Keywords: aggregation · fluorescence · π interactions · piezochromic materials · structure elucidation

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