

Layered Host–Guest Materials with Reversible Piezochromic Luminescence**

Dongpeng Yan, Jun Lu,* Jing Ma, Shenghui Qin, Min Wei,* David G. Evans, and Xue Duan

Luminescent materials sensitive to environmental stimuli are of great interest from both scientific and engineering aspects, due to their potential applications in fluorescent switches and optical devices.^[1] Pressure is one of the most common natural external stimuli, and thus pressure-induced chromic (known as piezochromic) luminescent (PCL) materials can be used to probe changes in pressure, especially under extreme conditions. To date, the study of PCL materials remains in its infancy compared with those of pH-, light- and temperature-sensitive materials.^[2–4] It has been recognized that one strategy to tune the fluorescence of a compound is to alter its molecular arrangement and packing mode since this can modify the intermolecular interactions.^[5–7] Although great efforts have recently been devoted to the study of pure organic fluorophores with PCL properties,^[8–10] the rational design and preparation of such materials remains a considerable challenge.

Materials with a two-dimensional (2D) layered structure, such as clays,^[11,12] are a large family of functional organized systems, characterized by tunable interlayer volume and variable interlayer guest. Recently, interest has focused on 2D clay-chromophore supramolecular hybrid materials, since they show novel functionality (such as enhanced photostabilization) which differ from those of their individual components.^[12] Importantly, the orientation and arrangement of the luminescent guest species can be tuned within the interlayer galleries of the 2D matrix, which facilitates the modulation of the luminescence properties of the fluorophore ensemble.^[3] Layered double hydroxides (LDHs) are one important type of layered matrix which exhibit a particularly large versatility by virtue of their tunable chemical composition and gallery space.^[13] The LDH sheets are sufficiently flexible to deform over intercalated bulky guests, and slipping of LDH sheets can occur on increasing the external pres-

sure.^[14] Based on the premise that a minor change in the molecular configuration can dramatically influence the host–guest interactions,^[15] we have fabricated a new type of PCL material by the assembly of an organic fluorophore (2,2'-(1,2-ethenediyl)bis[5-[[4-(diethylamino)-6-[(2,5-disulfophenyl) amino]-1,3,5-triazin-2-yl] amino]benzene sulfonate anion, denoted as BTZB, shown in Figure 1 a) into the interlayer galleries of LDH hosts. BTZB is a flexible long-chain stilbene derivative with four rotatable aromatic amine units, and thus its molecular conformation and intermolecular interactions can be tuned more easily by external perturbations than is the case for rigid molecules. It was found that the BTZB-intercalated LDH material exhibited optical responses to variations in external pressure, including changes in lumines-

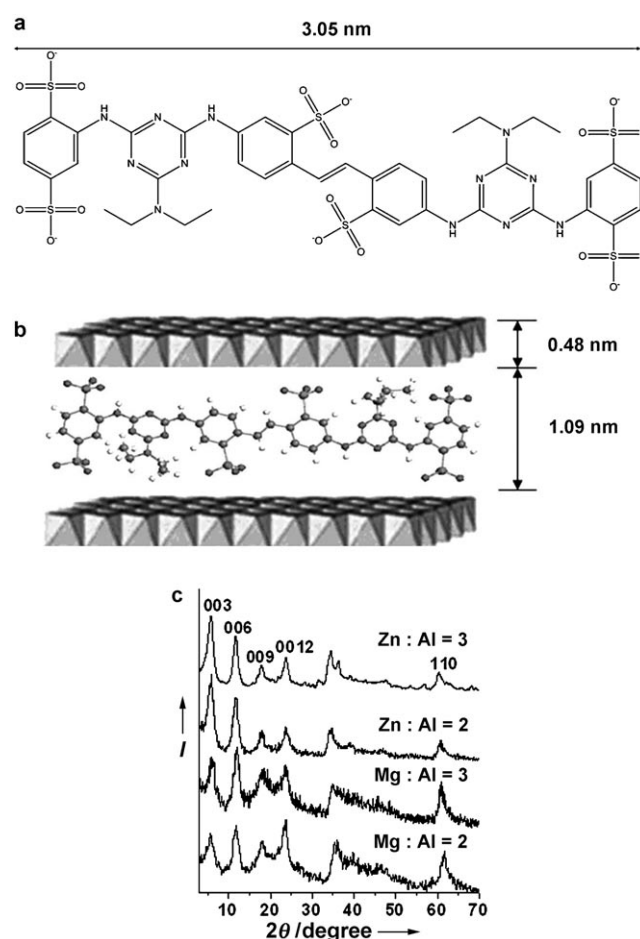


Figure 1. a) Molecular structure of BTZB; b) schematic view of the BTZB/Mg₂Al-LDH structure; c) XRD patterns of BTZB/MgAl-LDH (Mg:Al = 2:1 and 3:1) and BTZB/ZnAl-LDH (Zn:Al = 2:1 and 3:1).

[*] D. P. Yan, Prof. J. Lu, S. H. Qin, Prof. M. Wei, Prof. D. G. Evans, Prof. X. Duan
 State Key Laboratory of Chemical Resource Engineering
 Beijing University of Chemical Technology
 100029, Beijing (P.R. China)
 E-mail: lujun@mail.buct.edu.cn
 weimin@mail.buct.edu.cn

Prof. J. Ma
 School of Chemistry and Chemical engineering
 Nanjing University, 210093, Nanjing (P.R. China)

[**] This work was supported by the National Natural Science Foundation of China, the 973 Program (Grant No.: 2011CBA00504), the 111 Project (Grant No.: B07004).

Supporting information for this article (details of the preparation and computations for BTZB/LDHs) is available on the WWW under <http://dx.doi.org/10.1002/anie.201102232>.

cence color, UV/Vis absorption spectrum, and fluorescence lifetime. These PCL responses can be reversed by a grinding-heat treatment; thus, a tunable blue/green emission of the BTZB/LDH was obtained by varying external stimuli. Molecular dynamics (MD) and periodic density functional theoretical (PDFT) studies have demonstrated that the PCL performance originates from changes in the relative orientation and aggregation state of the interlayer BTZB. Since the pristine BTZB shows no PCL behavior at all, the transformation of a PCL-free organic fluorophore into a PCL material by incorporation into a layered matrix is the most distinctive feature of this work. The design strategy provides a promising method for assembling photofunctional guests into a 2D organized array and thus fabricating new PCL materials.

Four BTZB-intercalated LDH composites—BTZB/MgAl-LDH (Mg:Al=2:1 and 3:1) and BTZB/ZnAl-LDH (Zn:Al=2:1 and 3:1)—were prepared by a coprecipitation method.^[12] Elemental analysis (Table S1 and Figure S1 in the Supporting Information) showed that metal molar ratios in the products were very close to those in the corresponding synthesis mixture. Their XRD patterns are shown in Figure 1 c; all the reflections can be indexed to a hexagonal lattice with $R\bar{3}m$ rhombohedral symmetry. Taking BTZB/Mg₂Al-LDH as an example, the characteristic reflections appear at 5.64° (003), 11.38° (006), 17.77° (009), and 61.18° (110); the d_{003} (1.57 nm), d_{006} (0.75 nm), and d_{009} (0.50 nm) reflections show the expected relationship between the basal, second-order and third-order reflections. The basal spacing for the samples ranges from 1.51–1.57 nm, which is consistent with a single-layer arrangement of the BTZB in the LDH gallery (Figure 1 b). Moreover, the BTZB in the interlayer galleries of the LDH exhibits obvious differences in its FT-IR and ¹³C NMR spectra compared with the pristine BTZB, as shown in Figure S2 and S3 in the Supporting Information.

Both the pristine BTZB and BTZB/LDH composites show a blue luminescence with the maximum emission ($\lambda_{\text{max}}^{\text{em}}$) at approximately 452 nm. After a simple compression of the BTZB/LDH samples in an IR pellet press for 15 min at different pressures, a significant luminescent bathochromic shift occurred with a concomitant broadening of the emission band (Figure 2 a, Figure S4a–c in the Supporting Information). In marked contrast however, the emission spectra of pristine BTZB remain nearly unchanged under pressure (Figure S4d in the Supporting Information). The changes in fluorescence on varying the pressure were most obvious for BTZB/Mg₂Al-LDH: the $\lambda_{\text{max}}^{\text{em}}$ shifted from 452 to 515 nm on increasing the pressure from 0.1 MPa to 18.8 GPa (Figure 2 a,b). On increasing the pressure, the full width at half maximum (FWHM) of the fluorescence band showed a dramatic initial increase from 56 nm (0.1 MPa) to 95 nm (9.4 GPa), and then decreased to 84 nm (18.8 GPa, Figure S5 in the Supporting Information). Typical photographs of the BTZB/Mg₂Al-LDH pellet under UV light (Figure 2 a, inset) display a visual change in luminescence from blue to green with increasing pressure. The red-shift of the spectra can be attributed to the formation of *J*-type aggregates in the

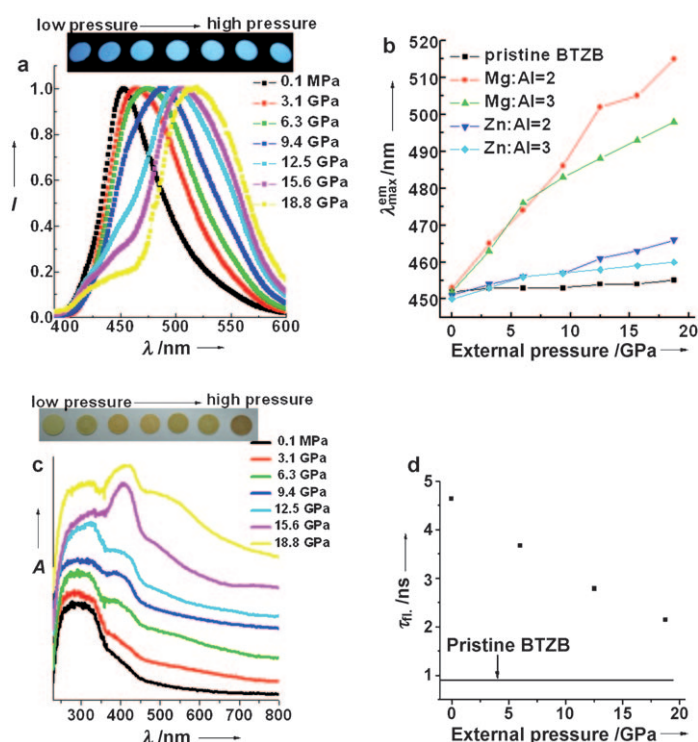


Figure 2. a) Fluorescence spectra of the BTZB/Mg₂Al-LDH at different pressures (inset: fluorescence photographs of pressurized samples under 365 nm UV light); b) $\lambda_{\text{max}}^{\text{em}}$ of BTZB/MgAl-LDHs (Mg:Al=2 and 3) and BTZB/ZnAl-LDHs (Zn:Al=2 and 3) at different pressures; c) UV/Vis spectra of the BTZB/Mg₂Al-LDH at different pressures; d) τ_{fl} for BTZB/Mg₂Al-LDH at four typical pressures.

interlayer galleries of the LDH, which is similar to the behavior of dyes intercalated into zeolite nanochannels.^[16] The PCL properties of BTZB/ZnAl-LDHs (Figure 2 b and Figure S4, S5 in the Supporting Information) are less marked than those of BTZB/MgAl-LDH, indicating that the chemical composition of the LDH layers has an influence on the PCL behavior of the interlayer BTZB.

An appreciable change in the UV/Vis absorption band of the BTZB/LDH composites was also observed on compression. For BTZB/Mg₂Al-LDH (Figure 2 c), the maximal absorption band occurred at approximately 290 nm under atmospheric pressure. On increasing the pressure, a new band ranging from 350–450 nm grew with increasing intensity. Furthermore, a broad shoulder band at 450–550 nm appeared when the pressure was increased to 15.6 GPa. This band can be assigned to the formation of *J*-type aggregates of BTZB in the LDH galleries,^[16a] consistent with the red-shift of the fluorescence spectra noted above. The color of BTZB/Mg₂Al-LDH changed from white-yellow to dark-yellow as the pressure was increased (inset in Figure 2 c). Similar behavior was also observed for the BTZB/Zn₂Al-LDH system (Figure S6 in the Supporting Information). XRD was carried out to obtain an insight into the influence of external pressure on the supramolecular organization of the host-guest system. Figure S7 in the Supporting Information displays the XRD patterns of the BTZB/Mg₂Al-LDH under four typical pressures. A decrease in the basal d_{003} spacing from 1.57 nm

(0.1 mPa) to 1.45 nm (18.8 GPa) can be detected upon compression. The contraction in gallery height can be expected to induce changes in the host-guest interactions and the arrangement and aggregation state of the guest anions, and thus influence the optical properties. Moreover, the relative intensity of the (006) reflection becomes lower than that of (003), suggesting that a realignment of the BTZB within the galleries of the LDH has occurred. To obtain information about the excited states of the BTZB/Mg₂Al-LDH, we further measured the fluorescence lifetimes (τ_{fl}) of different pressurized samples. The fluorescence decay process of the BTZB/Mg₂Al-LDH at high pressure was much faster than that at low pressure (Figure S8 in the Supporting Information). The fluorescence lifetime (Figure 2d) decreased from 4.63 ns (0.1 mPa) to 2.14 ns (18.8 GPa), further confirming the formation of aggregates of the fluorescent guests.^[16b]

Good reversibility and repeatability are important for practical application of PCL materials. When the compressed BTZB/Mg₂Al-LDH pellet sample was ground uniformly into a powder, heated at 100 °C for 3 min and then cooled down, the luminescence peak at 515 nm reverted to its original position of 452 nm (Figure 3a). This reversible luminescence color change can be readily repeated at least three times (inset in Figure 3a), and detected by the naked eye. The

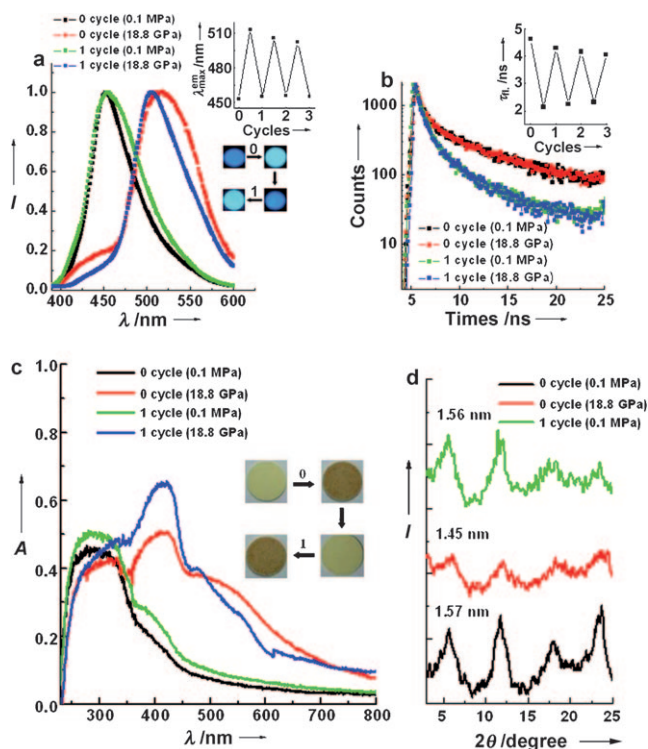


Figure 3. Reversible PCL of BTZB/Mg₂Al-LDH at two typical pressures (0.1 mPa and 18.8 GPa): a) changes in fluorescence spectra over two cycles (insets: the reversible λ_{max}^{em} response over three consecutive cycles; the photographs show luminescence changes over two cycles); b) the fluorescence decay curves (inset: τ_{fl} over three consecutive cycles); c) UV/Vis spectra over two cycles (inset: color changes over two cycles); d) the XRD patterns during a compression/grinding-heating cycle.

reversible changes in fluorescence decay and lifetime can also be repeated (Figure 3b), indicating that the luminescence properties of the BTZB/LDH can be switched at low and high pressures. The absorption spectra of the BTZB/LDH system also exhibited a reversible transformation (Figure 3c). Moreover, as shown in Figure 3d the contraction in basal spacing observed on increasing the pressure from 0.1 mPa to 18.8 GPa can be completely reversed by the grinding-heating treatment.

To study how the changes in configuration and aggregation state of the intercalated BTZB affect the luminescence properties when the material is subjected to external pressures, MD simulations^[17] were performed on an ideal BTZB/LDH model at six typical pressures from 0 to 25 GPa. The simulated d_{003} values decrease linearly with increasing pressure and the calculated values are very close to the experimental ones (Figure S9 in the Supporting Information). The simulated value of d_{003} returned to its original value over a pressure cycle (inset in Figure S9), in agreement with the XRD result. In addition, the long-axis direction of the BTZB anions is nearly parallel to the LDH sheets over the whole pressure range; the short-axis of the guest anions shows a tendency towards a tilted arrangement with respect to the LDH layer as the pressure increases (Figure S10a and 10b in the Supporting Information). Typical snapshots capturing the configuration under 0.1 mPa are shown in Figure 4. The most

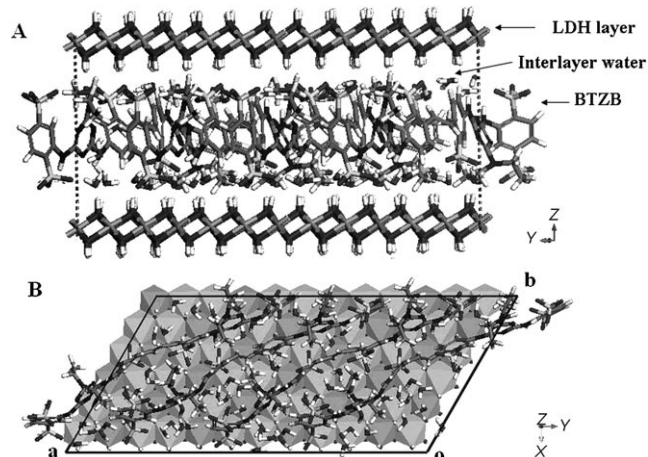


Figure 4. A) Side and B) top view of the BTZB/LDH structure models at 0.1 mPa.

probable relative orientation between adjacent BTZB anions increases from 34.3° to 40.0° as the pressure is increased from 0.1 mPa to 18.8 GPa (Figure S10c in the Supporting Information), indicating that only *J*-type aggregates of BTZB form in this pressure range. Furthermore, the central distance between neighboring BTZB anions (Figure S10d in the Supporting Information) decreases by approximately 7.5% at 18.8 GPa, compared with that at 0.1 mPa (0.94 nm). This result demonstrates that increasing the pressure induces a decrease in the distance between BTZB anions, which increases the contact probability and facilitates the formation of *J*-type aggregates. The BTZB also undergoes a dramatic

configuration change as the pressure is increased (Figure S11 in the Supporting Information). PDFT calculations^[17] show that for the pristine BTZB, the HOMOs and LUMOs are populated on the stilbene unit and its adjacent triazine groups (Figure S12a in the Supporting Information). Similar results were obtained for the BTZB/Mg₂Al-LDH under different pressures (Figure S12 in the Supporting Information), demonstrating that the luminescence originates from interlayer BTZB, and no energy transfer occurs between BTZB and the LDH layers. The band gap (Figure S13 in the Supporting Information) of BTZB/Mg₂Al-LDH decreases slightly on increasing the pressure. No obvious changes in the total electronic densities of states (TDOS) or partial electronic densities of states (PDOS) were observed on varying the pressure. For BTZB/Mg₂Al-LDH at 0.1 mPa (Figure S14 in the Supporting Information), the top of the valence band (TVB) and the bottom of the conduction band (BCB) are mainly dominated by the 2p(π) and 2p(π^*) C and N atomic orbitals derived from BTZB anions. Near the Fermi level, the TDOS are mainly contributed by the 2p electrons of C atoms in BTZB. The O 2p, Mg/Al 3s and the H 1s orbitals in the LDH layers contribute to the TDOS below the TVB and above the BCB. This suggests the LDH sheets inhibit the interaction between BTZB anions in adjacent interlayer galleries. It thus can be concluded that the PCL properties of the material are associated with the variations in orientation, configuration, aggregation state and packing mode of BTZB between the LDH layers.

In summary, layered PCL materials have been constructed by the intercalation of BTZB anions into the galleries of LDH. Unlike the pristine BTZB—which shows no PCL—the BTZB/LDH system exhibits a sensitive PCL response and reversible changes in fluorescence, optical absorption spectra, and structure in the pressure range 0.1 mPa–18.8 GPa. The reversible PCL of BTZB/LDHs suggests they have potential applications in luminescent sensors and switches. Theoretical calculations demonstrate that the PCL properties of BTZB/LDHs are related to the changes in packing mode, relative orientation, and configuration of the intercalated chromophores on compression. We anticipate that this approach

based on the incorporation of a bulky fluorophore into LDH interlayer galleries can also be effectively utilized to fabricate other novel PCL materials.

Received: March 31, 2011

Published online: June 17, 2011

Keywords: layered material · luminescence · molecular simulation · piezochromic materials · supramolecular chemistry

- [1] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **2002**, *420*, 759.
- [2] T. Mutai, H. Tomoda, T. Ohkawa, Y. Yabe, K. Araki, *Angew. Chem.* **2008**, *120*, 9664; *Angew. Chem. Int. Ed.* **2008**, *47*, 9522.
- [3] D. P. Yan, J. Lu, J. Ma, M. Wei, D. G. Evans, X. Duan, *Angew. Chem.* **2011**, *123*, 746; *Angew. Chem. Int. Ed.* **2011**, *50*, 720.
- [4] C. Löwe, C. Weder, *Adv. Mater.* **2002**, *14*, 1625.
- [5] T. Fukaminato, M. Irie, *Adv. Mater.* **2006**, *18*, 3225.
- [6] T. Mutai, H. Satou, K. Araki, *Nat. Mater.* **2005**, *4*, 685.
- [7] J. Kunzelman, M. Kinami, B. R. Crenshaw, J. D. Protasiewicz, C. Weder, *Adv. Mater.* **2008**, *20*, 119.
- [8] Y. Sagara, T. Mutai, I. Yoshikawa, K. Araki, *J. Am. Chem. Soc.* **2007**, *129*, 1520.
- [9] G. Zhang, J. Lu, M. Sabat, C. L. Fraser, *J. Am. Chem. Soc.* **2010**, *132*, 2160.
- [10] Y. Sagara, T. Kato, *Nat. Chem.* **2009**, *1*, 605.
- [11] T. J. Tambach, P. G. Bolhuis, B. Smit, *Angew. Chem.* **2004**, *116*, 2704; *Angew. Chem. Int. Ed.* **2004**, *43*, 2650.
- [12] D. P. Yan, J. Lu, M. Wei, D. G. Evans, X. Duan, *J. Phys. Chem. B* **2009**, *113*, 1381.
- [13] A. I. Khan, D. O'Hare, *J. Mater. Chem.* **2002**, *12*, 3191.
- [14] M.-A. Thyveetil, P. V. Coveney, H. C. Greenwell, J. L. Suter, *J. Am. Chem. Soc.* **2008**, *130*, 12485.
- [15] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabynyc, R. J. Kline, M. D. McGehee, M. F. Toney, *Nat. Mater.* **2006**, *5*, 328.
- [16] a) M. Busby, C. Blum, M. Tibben, S. Fibikar, G. Calzaferri, V. Subramaniam, L. D. Cola, *J. Am. Chem. Soc.* **2008**, *130*, 10970; b) M. Busby, A. Devaux, C. Blum, V. Subramaniam, G. Calzaferri, L. D. Cola, *J. Phys. Chem. C* **2011**, *115*, 5974.
- [17] See Supporting Information.