

Material Design for Piezochromic Luminescence: Hydrogen-Bond-Directed Assemblies of a Pyrene Derivative

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For more than a decade, tunable solid-state organic luminescent materials have been attracting considerable interest in various fields of application.¹ The tuning and switching of the luminescence of organic solids by controlling the mode of molecular packing instead of alteration of the chemical structure are attractive targets for both fundamental research and practical applications, but successful examples are quite limited and have been reported only recently.^{2,3} In this letter, we will present a novel material design for piezochromic luminescence based on a pressure-dependent mode of molecular packing. Piezochromism^{4,5} is the phenomenon of color change caused by mechanical grinding and reversion to the original color by heating or recrystallization, in which the presence of two different pressure-dependent stable or metastable states is essential.⁴ Up to now, organic piezochromic substances that show a color change by their luminescence are quite limited.⁶ Since luminescence can be detected with high sensitivity, materials that show piezochromic luminescence can find a wide variety of applications such as optical recording and strain- or pressure-sensing systems.

For a better understanding and prediction of molecular packing in organic crystals, Kitaigorodskii's close-packing principle⁷ and Etter's first hydrogen-bond rule⁸ are regarded as useful concepts and have been discussed extensively.⁹ Using these concepts as competing factors, we adopted a novel design principle to incorporate two strongly demanding factors for molecular packing, a planar aromatic core and multiple hydrogen-bonding sites, into a single molecular structure. The crystals of disk-shaped aromatics tend to be closely packed with an interplane distance of 0.34–0.36 nm,⁴ while hydrogen-bond-directed columnar assemblies have a wider interplane distance of 0.47–0.48 nm.¹⁰ The designed molecule, an amide-substituted tetraphenylpyrene derivative C6TPPy, successfully showed a piezochromic luminescence by pressure-induced alteration of the molecular packing and subsequent heating-induced restoration. This design principle is simple and applicable to developing a broad range of materials showing piezochromic luminescence.

1,3,6,8-Tetraphenylpyrene (TPPy) has a planar aromatic core and is a highly efficient fluorophore showing strong blue luminescence in solution (quantum yield $\Phi = 0.9$ in cyclohexane).¹¹ To the para position of the phenyl groups of this parent molecule, four hexyl amide units were introduced as the multiple hydrogen-bonding sites (C6TPPy, Figure 1a). The addition of methanol to a chloroform solution of C6TPPy resulted in precipitation of a white powder (B-form), which exhibited strong blue luminescence upon irradiation of UV-light (Figure 1b). Once the precipitate was formed, this B-form solid did not dissolve again in chloroform or other common organic solvents but dissolved only slowly in warm 1-methyl-2-pyrrolidinone. Interestingly, this blue-emitting white solid (B-form) was converted to a yellowish solid showing a strong greenish luminescence (G-form, Figure 1c) simply by pressing it with a spatula, and this change occurred only at the pressed area (Figure 1d). Grinding in a mortar thoroughly converted the B-form powder

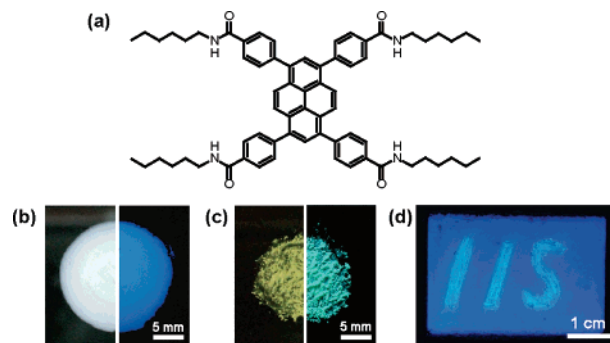


Figure 1. (a) Molecular structure of C6TPPy. (b) The B-form under room light (left) and under UV irradiation at 365 nm (right). (c) The G-form under room light (left) and under UV irradiation at 365 nm (right). (d) Luminescent image of the B-form solid cast on a glass plate after pressed with a metal block shaped 'IIS'.

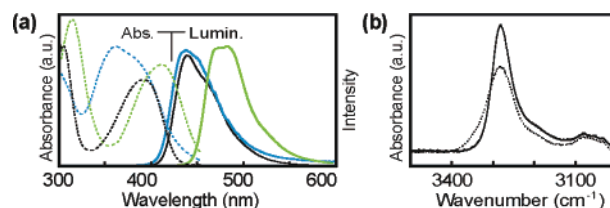


Figure 2. (a) Absorption and luminescence spectra of the B-form (blue), the G-form (green), and a chloroform solution (black; 1.0×10^{-5} M) of C6TPPy. (b) Infrared absorption spectra of the B-form (solid line) and the G-form (dotted line); normalized to the CH stretching peak at 2922 cm^{-1} .

to the G-form. This G-form solid after grinding readily dissolved in chloroform and reprecipitation from this solution gave the B-form powder again. This is a typical example of piezochromic luminescence.

A chloroform solution of C6TPPy showed structureless broad absorption and fluorescence bands ($\Phi = 0.7$, life time $\tau = 1.3$ ns) at 392 and 439 nm (Figure 2a), respectively, which are not much different from those of TPPy.¹² In the solid state, the emission band of the B-form ($\Phi = 0.3$, $\tau = 3.1$ ns) appeared at a position similar to that in solution, but the G-form solid showed considerable red-shifted emission at 472 nm ($\Phi = 0.3$, $\tau = 3.2$ ns). Tetraphenylpyrene derivatives are generally yellowish in color in the solid state showing blue-green to green luminescence, and the G-form solid falls in this category.¹³ It is noteworthy that the absorption band of the B-form solid appeared at the higher energy side, resulting in a white appearance. Since it is well documented that H-type aggregation in the columnar stacks induces a blue shift of the absorption, it is likely that the B-form solid has a columnar molecular assembly (see Supporting Information).

To clarify the different spectroscopic properties of these two solids, their solid-state structures were studied. The IR spectra of C6TPPy in the B- and G-forms were essentially the same, and the lower-shifted peak of the amide NH stretching at 3282 cm^{-1}

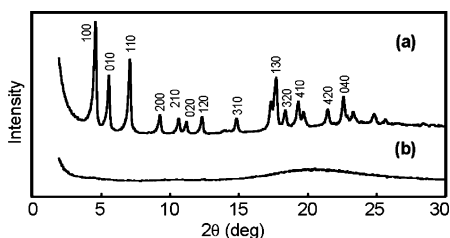


Figure 3. Powder X-ray diffraction patterns of C6TPPy: (a) the B-form obtained by reprecipitation from chloroform-methanol; (b) the G-form prepared by grinding the B-form solid.

indicated the formation of strong hydrogen bonds. Since no free amide NH stretching was observed at all, the amide units were fully hydrogen-bonded both in the B- and G-form solids. However, closer examination of the spectra revealed that the NH stretching peak of the G-form solid was apparently broader and extended to the higher wavenumber side (Figure 2b), indicating the presence of weakly hydrogen-bonded amide units. Therefore, the hydrogen bonds between the amide groups in the G-form were not in a uniform pattern but suffered a different extent of deformation by the applied pressure. A powder X-ray diffraction (XRD) pattern of the B-form solid (Figure 3a) showed clear reflection peaks, indicating that C6TPPy molecules in the B-form were packed in a relatively well-defined microcrystalline-like structure. The observed diffraction pattern can be interpreted by assuming a monoclinic or triclinic unit cell with $a = 1.90$ nm, $b = 1.57$ nm, and $\gamma = 93^\circ$, though the lattice parameter c is difficult to read from the diffraction pattern. The lattice parameters are well reproduced by a computational study on a columnar packing model of C6TPPy (see Supporting Information). Therefore, it is quite likely that the B-form solid has a columnar molecular assembly due to the quadruple hydrogen bonds, and the observed blue shift of the absorption band supports this conclusion. The estimated energy of the transition dipole interaction showed that the inter-ring distance of 0.48 nm is sufficient for inducing the observed blue shift of the absorption band if the rings are fixed by the quadruple hydrogen bonds (see Supporting Information). On the other hand, the G-form solid did not show any noticeable diffraction in the XRD profile (Figure 3b). The result indicated that the crystalline-like ordered structure of the B-form was disrupted in the G-form solid, agreeing well with the IR results.

The thermal properties of the solids were studied by differential scanning calorimetry (DSC). Though the heating profile of the B-form solid showed no peak up to 250 °C, a clear exothermic peak at 111.6 °C was observed only in the first heating curve of the G-form solid. From microscopic observation, this thermal behavior was ascribed to a solid–solid transition with simultaneous luminescence color change to blue. Since the XRD pattern of the heated sample was quite similar to that of the initial B-form solid, the G-form solid was converted exothermically to the more stable B-form by heating above the transition temperature (see Supporting Information). Thus, these results confirmed the rewritable nature of the C6TPPy solid, that is, writing by pressing or grinding to the green-emitting state and erasing by heating to the blue-emitting state, and this cycle was well reproducible.

Quite recently, Oyamada et al.¹⁴ reported that solid-state TPPy purified by sublimation showed blue emission, which turned to

green after thermal annealing, suggesting the importance of the solid-state arrangement of the luminophores. In our study, we showed the critical role of the quadruple amide hydrogen bonds for construction of the well-defined columnar assembly in the blue-emitting B-form solid. Intermolecular amide hydrogen bonds contributed to the stability of this form under an ambient condition, showing that the B-form has the hydrogen bond-directed structure. Applied pressure to the B-form solid caused disruption of the columnar structure and yielded the G-form solid with the poorly ordered molecular packing. Since disruption of the columnar packing resulted in a different luminophore arrangement within the solid, it is not surprising that the G-form solid showed greenish luminescence. Thus, the design principle of introducing the planar fluorescent aromatic core and the multiple hydrogen-bonding sites within the same molecular structure was shown to be effective for designing materials displaying piezochromic luminescence. Our preliminary study on a perylene derivative having two amide side chains also showed change in luminescence upon grinding, though thermal reversion was not observed in this case. Therefore, the design principle we adopted here could be widely applicable to other molecular systems.

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Supporting Information Available: Synthesis, characterization, DSC analysis, molecular modeling of C6TPPy, and an effect of transition dipole interaction in the solid state. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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