Design of Amorphous Molecular Materials and Their Emitting Properties

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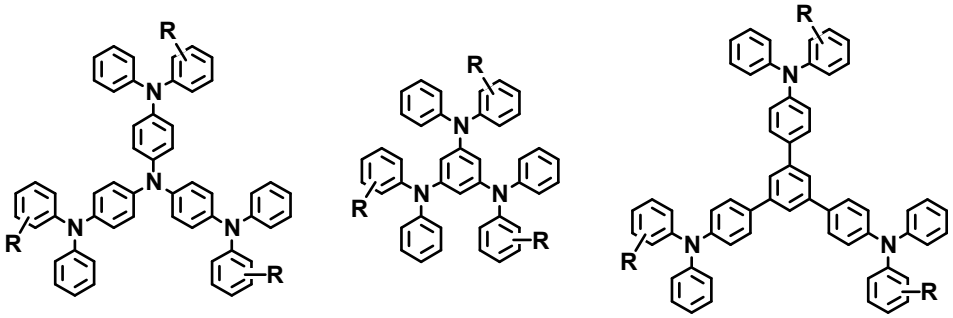
Low molecular-mass materials that readily form amorphous glasses above room temperature are referred to as "amorphous molecular materials". From 1990s, studies on creation of novel photo- and electro-active amorphous molecular materials were actively made in Prof. Y. Shirota's group in Osaka University and more than one hundred kinds of amorphous molecular materials have been created. Charge-transporting and emitting amorphous molecular materials have been investigated to be applied for use in organic electroluminescent devices. Recently, we have found that several emitting amorphous molecular materials exhibited mechanochromic emission. Here, basic concept of molecular design for amorphous molecular materials and our recent progress of the studies on mechanofluorochromic amorphous molecular materials will be presented.

Design of Amorphous Molecular Materials[1)]

In the initial stage of the studies on the creation of amorphous molecular materials, a series of π-electron starburst molecules shown in Chart 1 were designed and synthesized, and it was found that these molecules could easily form stable amorphous glasses above room temperature when the melt samples were cooled either rapidly by liquid nitrogen or slowly on standing in air. Since then, a variety of amorphous molecular materials have been designed and synthesized. It was suggested that glass-forming ability can be added relatively easily by introducing a propeller-like skeleton with a non-planar structure, such as triphenylamine, tris(diarylamino)benzene, or triphenylbenzene, into the molecule.



TDATA : R = H
o-MTDATA : R = *o*-CH_3
m-MTDATA : R = *m*-CH_3
p-MTDATA : R = *p*-CH_3

(TDAB : R = H)
o-MTDAB : R = *o*-CH_3
m-MTDAB : R = *m*-CH_3
p-MTDAB : R = *p*-CH_3

TDAPB : R = H
o-MTDAPB : R = *o*-CH_3
m-MTDAPB : R = *m*-CH_3
p-MTDAPB : R = *p*-CH_3

Chart 1. Starburst Molecules for Amorphous Molecular Materials

However, highly symmetric molecule might not allow to form amorphous glass. For example, TDAB with a non-planar but rather symmetric structure crystallizes easily and does not form an amorphous glass.

The control of the glass transition temperature (Tg) is also important in the design of amorphous molecular materials. Tg can be improved by introducing a rigid skeleton such as carbazolyl, thiazolyl, naphthyl, and fluorenyl groups into the molecule.

Mechanofluorochromic Amorphous Molecular Materials

The phenomena of reversible changes in emission color induced by mechanical stimuli are referred to as "mechanochromic emission" or "mechanofluorochromism" and have recently attracted much attention. We have reported that the amorphous molecular material, BMABA, exhibited mechanochromic emission.[2] While the recrystallized sample of BMABA exhibited blue-violet fluorescence, the emission color turned to yellow-green by mechanical grinding, and returned to the original on standing. BMABA was thought to take TICT structure in the excited state, however it emitted in shorter wavelengths region in the crystalline state because it cannot relax its structure upon excitation. On the other hand, in the amorphous state obtained by mechanical grinding, relaxation to take TICT structure was allowed to emit in longer wavelength region. Since the Tg of BMABA was lower than room temperature (8 °C), the amorphous state after grinding was unstable and crystallization took place gradually, so the luminescent color returned to the original on standing. BMAAP (Tg: 9 °C) exhibited similar mechanochromic emission,[3] whereas BFABA with higher Tg of 67 °C was stable in the amorphous state so that yellow-green emission obtained by mechanical grinding could be stored for a long time at room temperature.[4] BMBZA and BMZPy exhibited OFF-ON and ON-OFF type mechanochromic emissions, respectively.[5]

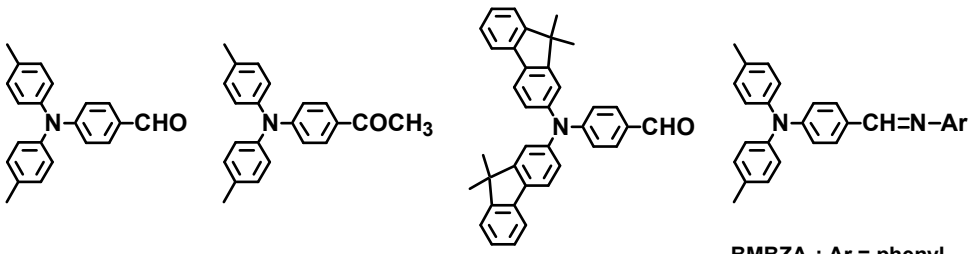


Chart 2. Amorphous molecular materials exhibiting mechanochromic emission.

References

1) Y. Shirota, *J. Mater. Chem.*, **10**, 1 (2000); *J. Mater. Chem.*, **15**, 75 (2005) and references sited therein. 2) H. Nakano et al., *Mater. Lett.*, **65**, 2658 (2011). 3) H. Nakano et al., *J. Photopolym. Sci. Tech.*, **27**, 535 (2014). 4) H. Nakano et al., *Dye Pigm.*, **96**, 76 (2013). 5) H. Nakano et al., *Rapid Commun. Photosci.*, **3**, 38 (2014).