White light emissive molecular siblings

Human eye is capable of detecting only a relatively tiny part of the electromagnetic spectrum. However limited our vision might be, it is filled with the experiences of numerous colors, colors that control our emotional responses. White-light can be regarded as a balanced composition of red (R), green (G), and blue (B) colors and can be realized in infinite ways. Generation of white-light in luminescent materials is a challenging task. Practical observations and theoretical knowledge suggest that such broad emission from a single molecular system is seldom possible because fluorophores always tend to undergo vibrational relaxation in their excited states resulting in single-color emission of possible lowest energy excited state (Kasha's rule). There are only a few reports in which Kasha's rule is apparently broken. Strategies based on ESIPT (excited-state proton transfer), symmetry breaking, doping in composite structures are also used for generation of such broad range RGB luminescence.

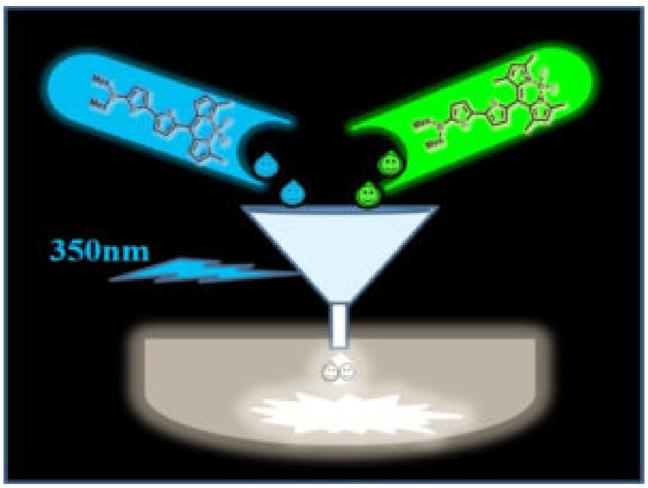

Fig. 1. Tricolor emissive triad (1), Molecular structure of 2 and 3 (Left). Schematic representation of the concept used in generation of white-light (right)

Very recently, we have shown that the combination of triarylborane and boron dipyromethene (BODIPY) units in a single molecule can result in previously unexplored broad range emission profiles. Encouraged by these results, we have designed a novel molecular triad containing bithiophene, TAB and BODIPYunits (Fig. 1, compound 1), which showed intriguing tricolor (RGB) emission, rarely observed in any given molecular system. However, the relative intensity ratio of the luminescent peaks is not complementary enough to produce white light. Two fluorescent compounds with similar absorption profiles and complementary luminescent colors can be regarded as the ideal couple for the generation of white-light as intermolecular FRET processes should be negligible preventing any practical loss of fluorescence efficiency. Making use of this new conceptual framework, we engineered molecular siblings 2 and 3 with analogous absorption spectra and complementary luminescence features.

Compounds 2 and 3 show dual emission upon photo excitation at the triarylborane dominated absorption region. Spectral investigations clearly indicate that the observed dual emission bands arise as a result of partial energy transfer from borane to BODIPY unit. The relative intensity ratios of the luminescent peaks of both 2 and 3 are significantly different. The emission of compound 2 is dominated by blue color while that of 3 by green color. This difference can be attributed to the different degree of electronic energy transfer in these molecular siblings. In molecular systems, the energy transfer process would be efficient when both donor and acceptor luminophores lie in the same plan. Such coplanar arrangement of luminophores is more favored in 3 than in 2. Hence, better energy transfer efficiency is observed for 3 compared to 2.

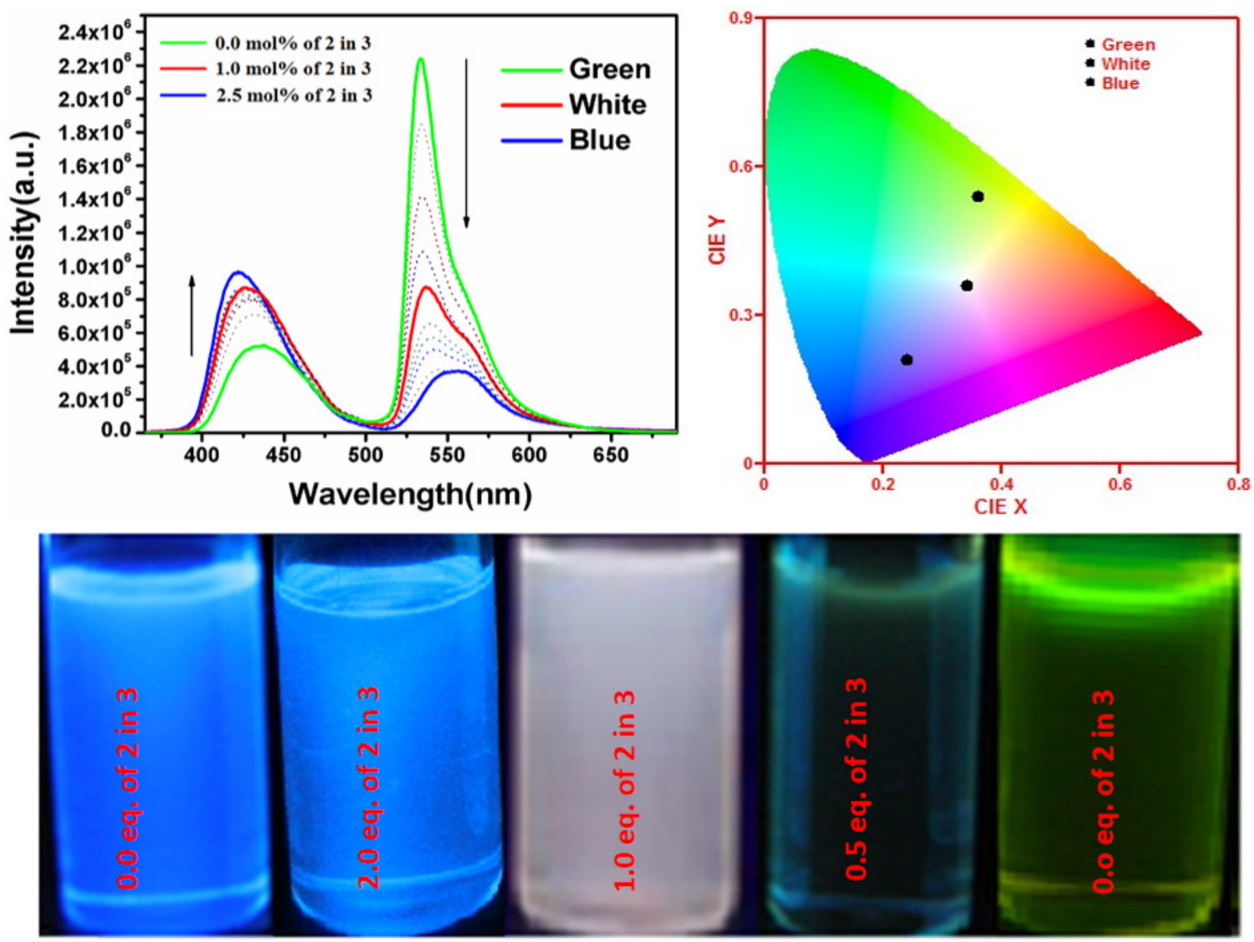

Fig. 2. Fluorescence spectra of mixture of 2 and 3, in different ratio (top, left), CIE diagram (top, left), Photographs of different color emission from different molar ratio of 2 and 3 in CH2Cl2 under UV light (365 nm).

To rationalize our new concept of generating white light by mixing molecular siblings having complementary emissive features, compounds 2 and 3 were mixed in different ratios and the luminescence behavior was monitored. Mixtures of 2 and 3 in different ratios produced different colors such as blue, green etc. However, an equimolar mixture of 2 and 3 emitted white color when excited at 350 nm. The observed CIE (Commission Internationaled'Eclairage) coordinates (0.34, 0.34) match well with the CIE coordinates of the natural white light (0.33, 0.33). Interestingly the binary mixture of solids of 2 and 3 also produce white light; however the emission quantum yields are lower compared to those observed in solutions. These results represent a significant major advance in the development of white light emissive materials. And will be useful in making small molecule based full color OLEDs.

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