Comparative computational study of C-N and C-C bonding visible to NIR absorbing croconines

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Lowest electronic excitations in two series of croconine dyes; 1) with C–N bonding molecules having absorption in visible region (400–600 nm) and 2) with C–C bonding molecules showing absorption in visible to near infrared (NIR) region (600–900 nm) are analyzed with DFT, TDDFT and SAC-CI methods. The lowest electronic excitations in C-C bonding croconines (CCR) are always having 200–300 nm red shifted absorption than its corresponding C-N bonding croconines (NCR). The reason for this drastic red shift in CCR series than its corresponding NCR has been systematically studied and found that, CCR series are with less charge transfer in nature and are having larger diradical character, whereas NCR series molecules are showing larger charge transfer with lower diradical character. The change in bonding mode of croconate from C–N to C–C, destabilization of HOMO and stabilization of LUMO was observed. Due to the stabilization and destabilization of LUMO and HOMO levels respectively in CCR molecules, these are having larger red shifted absorption than NCR molecules. This study may helpful in design and synthesis of new visible to NIR absorbing croconine dyes which are useful in materials applications.

Fig. 1. Structure of C-N bonding (NCR) and C-C bonding (CCR) croconines.

Keywords: visible to NIR absorbing croconines, diradical character and C-N & C-C bonding croconines

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