

## Twisted $\pi$ -System Chromophores. Progress and Prospects

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Twisted intramolecular charge transfer (TICT) chromophores are composed of electron-donating and electron-accepting  $\pi$ -substituents joined by a sterically constrained twisted bi-aryl fragment. In such chromophores, the twisting of the  $\pi$ -system enforces charge separation in the electronic ground state, leading to large dipole moments and strong, low-lying charge-transfer excitations. This unique electronic structure forms the basis for enhanced NLO response, with an archetypal TICT chromophore, **TMC-2**, exhibiting very large second order metrics,  $\mu\beta = 24,000 \times 10^{-48}$  esu (other chromophores even larger), and third order,  $\gamma = 1.4 \times 10^{-33}$  esu, in dilute low-polarity solutions. This lecture summarizes several approaches to enhance  $\mu\beta$  in various environments, including; (1) manipulating the bi-aryl torsional angle; (2) modifying the electron accepting fragment; (3) extending conjugation; (4) adding multiple twisted fragments; (5) modifying chromophore sidechains; (6) tuning the chromophore environment. Another set of modifications is explored to enhance  $\gamma$ : (1) coupling to a cyanine dye to hybridize the cyanine and TICT orbitals; (2) manipulating the donor and acceptor group identity. As a result of the extensive modifications described above, detailed understanding of TICT chromophore molecular response emerges as does the unambiguous evidence such chromophores have the potential to revolutionize organic electro-optics.