

# **Large dynamic Stokes shift of DNA intercalation dye Thiazole Orange, from twisting coupled with a high-frequency mode**

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Fluorescence of the cyanine dye Thiazole Orange (TO) is strongly quenched by intramolecular twisting in the excited state. In polynucleotides a progression from a  $1400\text{ cm}^{-1}$  mode depends on base pairing, which suggests that twist and high-frequency displacement are coupled. This hypothesis is confirmed with TO in methanol by femtosecond fluorescence upconversion and transient absorption spectroscopy. Emission from the Franck-Condon state shifts to the red by  $1000\text{ cm}^{-1}$  and broadens during 200 fs. The radiative rate does not decrease during this initial period. Vibronic structure at 300 fs is assigned to asymmetric stretching activity in the methine bridge. Further Stokes shift and decay are observed over 2 ps. Emission from the global  $S_1$  minimum is discovered in an extremely wide band around  $12000\text{ cm}^{-1}$ . As the structure twists away from the Franck-Condon region the mode becomes more displaced and better overlap with ground-state wavefunctions is achieved. Twisting motion is thus leveraged into a fast-shrinking energy gap and internal conversion ensues.