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A Comprehensive Study of Structure-Property Relationships for Two-photon Absorbing Triarylamine Molecules Containing Trifluoromethyl

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This work reports on the influence of the Electron Withdrawing Groups (EWG) strength on the one- and two-photon absorption properties of six novel push-pull triarylamine molecules containing trifluoromethyl (CF_3). The molecules present octupolar structures with a core based on triarylamine (strong donor group) containing two trifluoromethyl-phenyl arms (acceptor group) and another with distinct EWG strength (H < CN < CHO < NO2 < Cyet < Vin). Linear photophysical properties such as molar absorptivity, one-photon induced fluorescence, solvatochromic Stokes shift measurements, dipole moments, fluorescence quantum yield and lifetimes were investigated using several spectroscopic techniques. For the two-photon absorption measurements we used the open-aperture Z-scan technique with femtosecond pulses operating at low repetition rate (1 KHz). Our results point out that the 2PA cross-section is enhanced and redistributed more homogeneously along the nonlinear spectrum as a function of increase of the EWG strength. More specifically, the 2PA cross-section is enhanced of 40 up to 125 GM for the lowest energy band and 95 up to 265 GM for the high energy band. These results were elucidate from the large changes observed in transition and permanent dipole moment as consequence of (i) increase of the EWG strength, (ii) improve the electronic coupling among the arms and (iii) higher planarization of triarylamine core. We apply two and three-energy level approximation to establish a quantitative relation between the 2PA and the molecular properties of the chromophores in solution. This relation is elucidated by comparing $\Delta\mu$ values obtained from the 2PA

measurements with quantum-chemical calculations and with measurements of solvatochromic shifts in a series of solvents. Moreover, it has been found that the 2PA cross-section normalized by the molecular weight for these compounds are considerably higher than to others triarylamine derivatives with similar molecular structures. We attributed this result to presence of the CF_3 group that provides new charge transfer excited states from the amino core towards the biphenyl groups. The 2PA results were supported and confronted with theoretical predictions of the two-photon transitions strengths, provided by response function calculations within the density functional theory (DFT) framework.