

The aim of this work was to study the photophysics in a series of (alkyl)amino substituted phthalides (APds) as a function of the substituent position in aprotic media of various polarity. Various substitution position of the amino group against the carbonyl group of the phthalide (Pd) skeleton (*ortho*, *meta* and *para*-isomers) and its structural modification (primary, secondary and tertiary amines) provide good comparative background to study their photophysical properties in solvents of different polarity and proticity.

In the present work, systematic spectroscopic studies with steady-state UV-Vis absorption, fluorescence and time-resolved fluorescence techniques were supported by the extensive quantum-chemical calculations of the ground and excited states using CASSCF and TD DFT methods. Special attention has been paid to describe the excited state: its structure, excited state dipole moment ($\bar{\mu}_e$) and the deactivation pathway.

In all non-*para* APds (*ortho* and *meta*-APds) the lowest excited state is of an intramolecular charge transfer (CT) character. The charge transfer in these isomers is almost accomplished directly during absorption. The following excited state vibrational relaxation does not involve strong conformational changes and only slightly increases the charge separation. This has been supported by the excited state TD DFT and CASSCF calculations on these APds. The calculations indicated significant angular displacement of the $\bar{\mu}_e$ vector against the $\bar{\mu}_g$, pointing to CT towards *meta* and *ortho* positions of the benzene ring. The dependence of the Stokes shift on the solvation as well as high fluorescence quantum yields and long radiative decay times make non-*para* APds good candidates for fluorescent probes for long-time scale molecular dynamics.

In a series of *para*-APds (5-APds) the S_1 and S_2 states are closely lying: $\Delta E(S_1-S_2)$ is within 0.25 eV for all derivatives, as indicated by TD DFT calculations. This makes the nature of the emitting state in 5-APds dependent on the polarity of surroundings which is proven by significant increase (by ~ 1.5 times from *n*-hexane to acetonitrile) of the emission transition dipole moment. The combination of strong electron donating ability of amino substituent, its high flexibility (5-DMAPd), and medium polarity enhances this effect. 5-DMAPd in moderately and strongly polar media emits second, low-energy fluorescence from a highly polar state. Dual luminescence of 5-DMAPd in moderately and strongly polar media was explained in terms of twisted intramolecular CT (TICT) state model.

In protic media the non-*para* APds are complexed by solvent molecules in the ground state, which leads to enhancement of nonradiative depopulation upon electronic excitation. In *para*-APds almost no ground state complexation occurs, due to relatively strong coupling of the nitrogen lone pair with π -electronic system of the Pd moiety.

The extensive excited state TD DFT quantum chemical calculations provide a detailed picture of the excited state of APds studied: the geometry, the $\bar{\mu}_e$ value as well as the absorption and emission transition energies. The theoretically obtained values are in good agreement with their experimental counterparts. Exploring the possibility of the excited state relaxation through the population of dissociative $^1(\pi,\sigma^*)$ state in a series of *meta*-APds (6-APds) with CASSCF method gave a negative result: the energy barrier between the $^1(\pi,\pi^*)$ (CT) and the $^1(\pi,\sigma^*)$ states is too high: ~ 1.1 eV.