Supporting information for

Decoding Structural Rigidity and Charge-Transfer Polarization in Barbituric-Acid-Based Donor–π–Acceptor Chromophores

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Computational Details

All quantum chemical calculations were performed using the Gaussian 8 software package. The ground-state (S_0) geometries of compounds 1 and 2 were fully optimized using Density Functional Theory (DFT) at the B3LYP/6-31G(d) level of theory without imposing any symmetry constraints. Frequency calculations were subsequently carried out at the same level to confirm that all optimized structures correspond to true minima on the potential energy surface, as evidenced by the absence of imaginary frequencies.

Excited-state (S_1) geometries were optimized using Time-Dependent Density Functional Theory (TD-DFT) at the same level of theory (B3LYP/6-31G(d)). Vertical excitation energies, oscillator strengths (f), and electronic transition characteristics were obtained from TD-DFT calculations based on the optimized ground-state geometries.

To investigate solvent effects, the Polarizable Continuum Model (PCM) was employed using the integral equation formalism variant (IEF-PCM). Calculations were performed in representative solvents of varying polarity. Both ground-state and excited-state properties were evaluated within the PCM framework to assess dielectric stabilization and solvent-dependent modulation of electronic structure.

Frontier molecular orbital (FMO) analysis was conducted using the optimized ground-state geometries to obtain HOMO and LUMO energy levels and spatial distributions. The HOMO–LUMO energy gap (ΔE) was calculated directly from orbital energies.

Atomic charge distributions were analyzed using both Mulliken population analysis and Natural Population Analysis (NPA) as implemented in the NBO 3.1 module integrated within Gaussian 8. Electrostatic potential (ESP) surfaces were mapped onto electron-density isosurfaces (0.001 a.u.) to visualize charge distributions and polarization characteristics.

Conceptual DFT (CDFT) global reactivity descriptors were calculated using frontier orbital energies in accordance with Koopmans' theorem. The ionization potential (I) and electron affinity (A) were approximated as:

$I = -E$ HOMO and $A = -E$ LUMO.

From these values, the following descriptors were computed:

1. Chemical potential: $\mu = -(I + A)/2$
2. Electronegativity: $\chi = (I + A)/2$

3. Global hardness: $\eta = (I - A)/2$
4. Global softness: $S = 1/(2\eta)$
5. Electrophilicity index: $\omega = \mu^2/(2\eta)$

Electron-donating (ω^-) and electron-accepting (ω^+) powers, as well as the charge-transfer descriptor (ΔN), were evaluated using standard formulations reported in the literature.

Dipole moments and thermodynamic parameters, including Gibbs free energy (G), enthalpy (H), and entropy (S), were obtained from frequency calculations under gas-phase and PCM conditions.

The isotropic polarizability (α iso) and polarizability tensor components were extracted from the Gaussian output files to assess the electronic deformability and anisotropy of the molecular systems.

Additional figures

Compound	Donor atom	NBO charge (e)	Key acceptor atoms	NBO charge (e)	Interpretation
1	N17	-0.414	O26	-0.615	weak donor to acceptor polarization
1			O27	-0.612	
1			O28	-0.621	
1			N29	-0.678	
2	N5	-0.677	O28	-0.583	stronger donor to acceptor polarization
2			O30	-0.552	
2			N32	-0.682	

Table S1: Charges obtained from Natural Population Analysis at the B3LYP/6-31G(d) level.