# Substituent Effects on the Solubility and Electronic Properties of Dyes: Density Functional and Time-Dependent Density Functional Theory Calculations

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## 1. Introduction and Motivation

- Dyes have been shown to exhibit molecular aggregation and exciton delocalization [1-3]. Dye aggregation can be facilitated and controlled using DNA templating [3-4].
- Exciton dynamics depend on dye aggregation, monomer transition dipole moments ($\mu$), and static dipole differences ($\Delta d$) [5].
- We studied the effects of electron donating and electron withdrawing substituent pairs (quantified using Hammett constants, $\sigma_p$) on the solubility and electronic properties of the cyanine dye Cy5 (Fig. 1).
- Desirable properties: greater hydrophobicity for denser dye packing, large $\mu$ and $\Delta d$ for enhanced excitonic function.
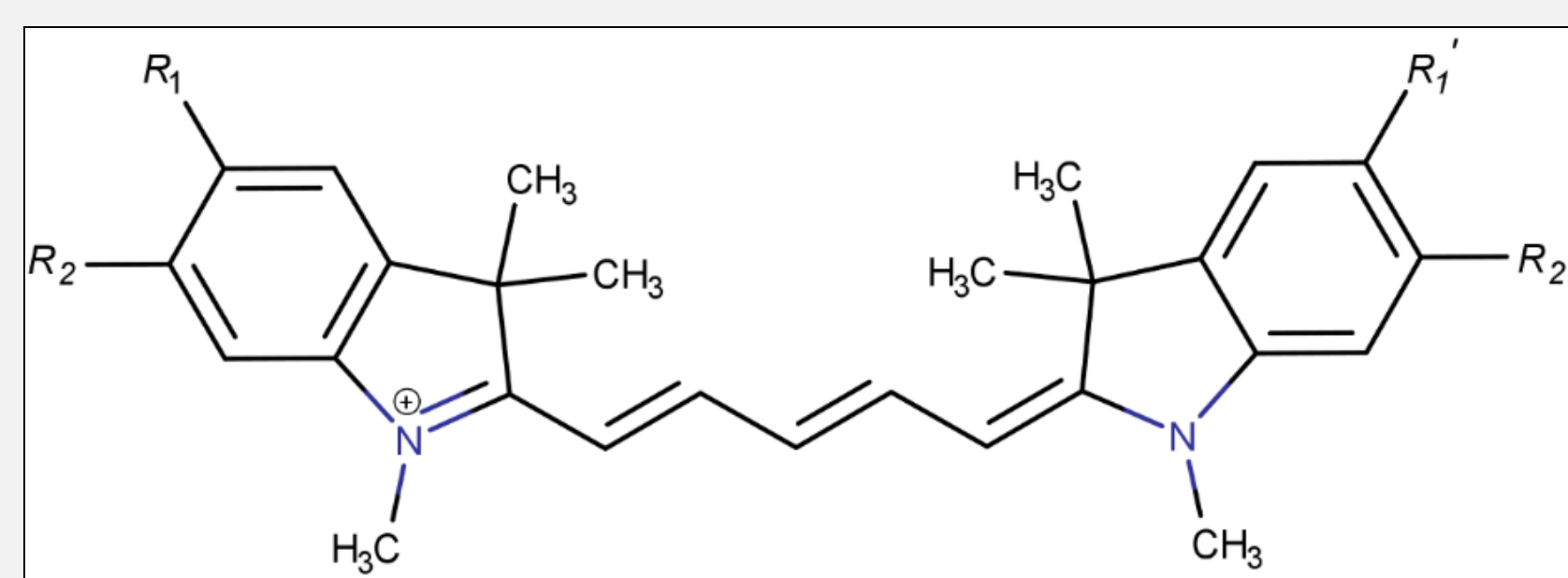


**Figure 1**. Molecular structure of the cyanine dye Cy5. Hydrogens at 'R' locations replaced with substituents.
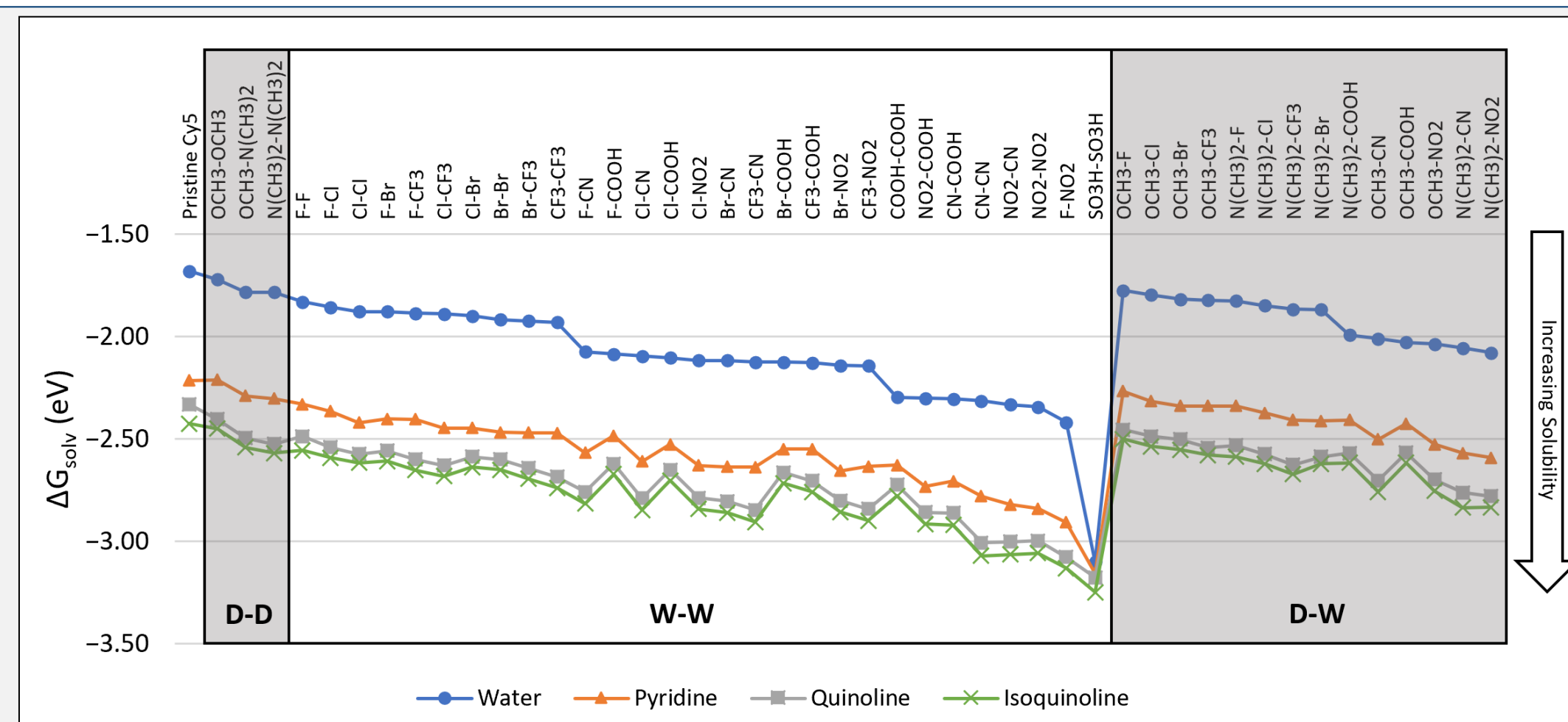
## 2. Computational Methods

- Density functional theory (DFT) was used to optimize the dyes in the ground state and time-dependent (TD-) DFT was used to calculate vertical excited state properties [6].
- Used pairs of electron donating substituents (D-D), pairs of withdrawing substituents (W-W), and pairs of one donating and one withdrawing substituent (D-W) attached at 'R' sites in Fig. 1.
- Calculations done in vacuum, water, pyridine, quinoline, and isoquinoline. Pyridine, quinoline, and isoquinoline were used to approximate the effects of a DNA environment.
- Solubility approximated with solvation energy ($\Delta G_{solv}$, Eq. 1), where $E_{solvated}$ is the total energy of the solvated dye and $E_{vacuum}$ is the total energy of the dye in vacuum [7].
- $\Delta d$ was calculated using Eq. 2, where $d_i^j$ is the Cartesian dipole moment vector component, i is the Cartesian direction, and j is either GS or ES (ground state or excited state) [8].

$$\Delta G_{solv} = E_{solvated} - E_{vacuum} \quad (1)$$

$$\Delta d = \left[ \left( d_x^{ES} - d_x^{GS} \right)^2 + \left( d_y^{ES} - d_y^{GS} \right)^2 + \left( d_z^{ES} - d_z^{GS} \right)^2 \right]^{\frac{1}{2}} \quad (2)$$

| Substituent | $\sigma_p$ | Classification |
|---|---|---|
| N(CH₃)₂ | −0.83 [a] | Donating |
| OCH₃ | −0.27 [a] | Donating |
| F | 0.06 [a] | Withdrawing |
| Cl | 0.23 [a] | Withdrawing |
| Br | 0.23 [a] | Withdrawing |
| COOH | 0.45 [a] | Withdrawing |
| CF₃ | 0.54 [a] | Withdrawing |
| SO₃H | 0.64 [b] | Withdrawing |
| CN | 0.66 [a] | Withdrawing |
| NO₂ | 0.78 [a] | Withdrawing |

## 3. Results and Discussion, Part A



**Figure 2**. Solvation energies of substituted Cy5 dyes in water, pyridine, quinoline, and isoquinoline solvents calculated using Eq. 1. Lines added to the data are to highlight trends and are not meant to infer quantitative behavior.
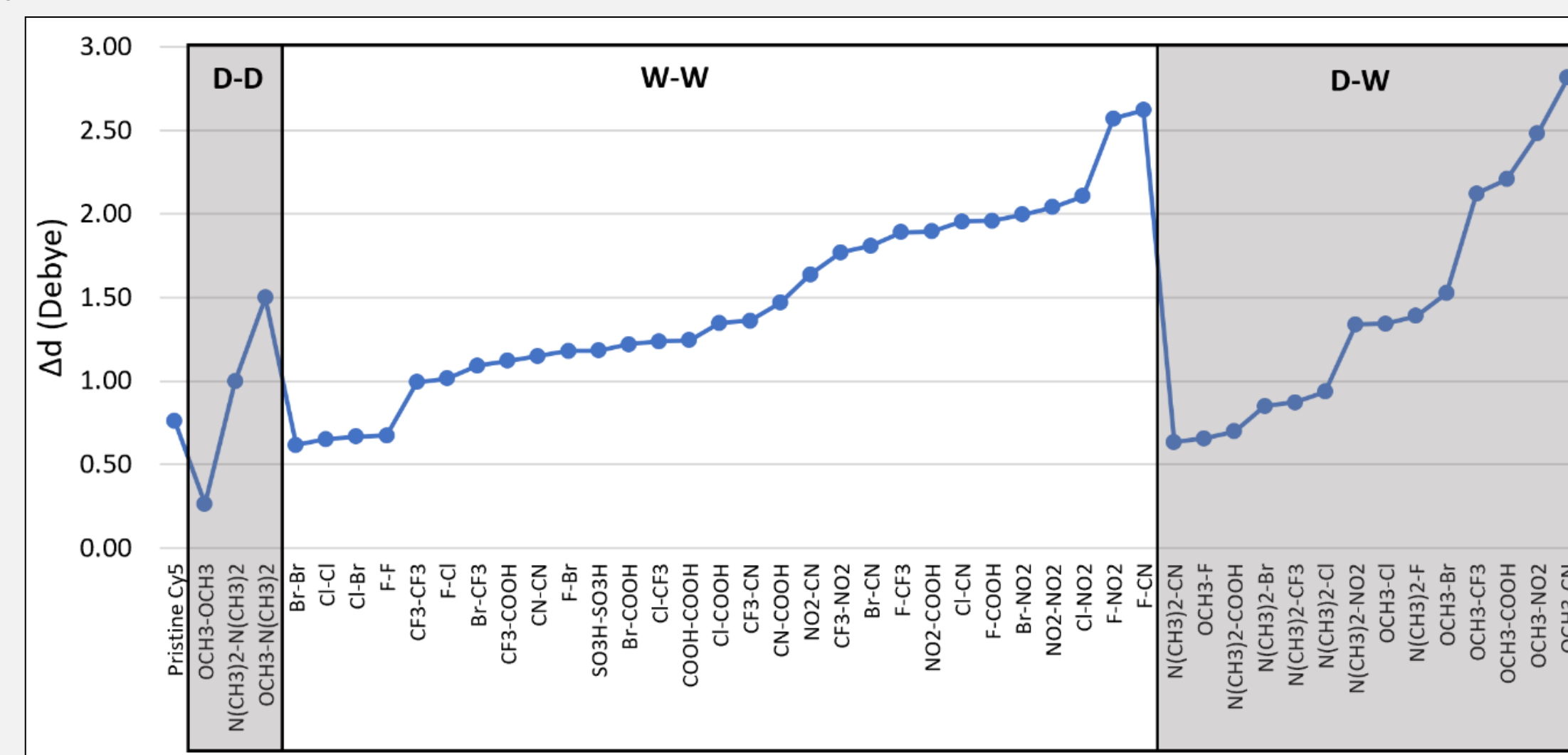


**Figure 3**. Static dipole differences of substituted Cy5 dyes in water calculated using Eq. 2. Lines added to the data are to highlight trends and are not meant to infer quantitative behavior.
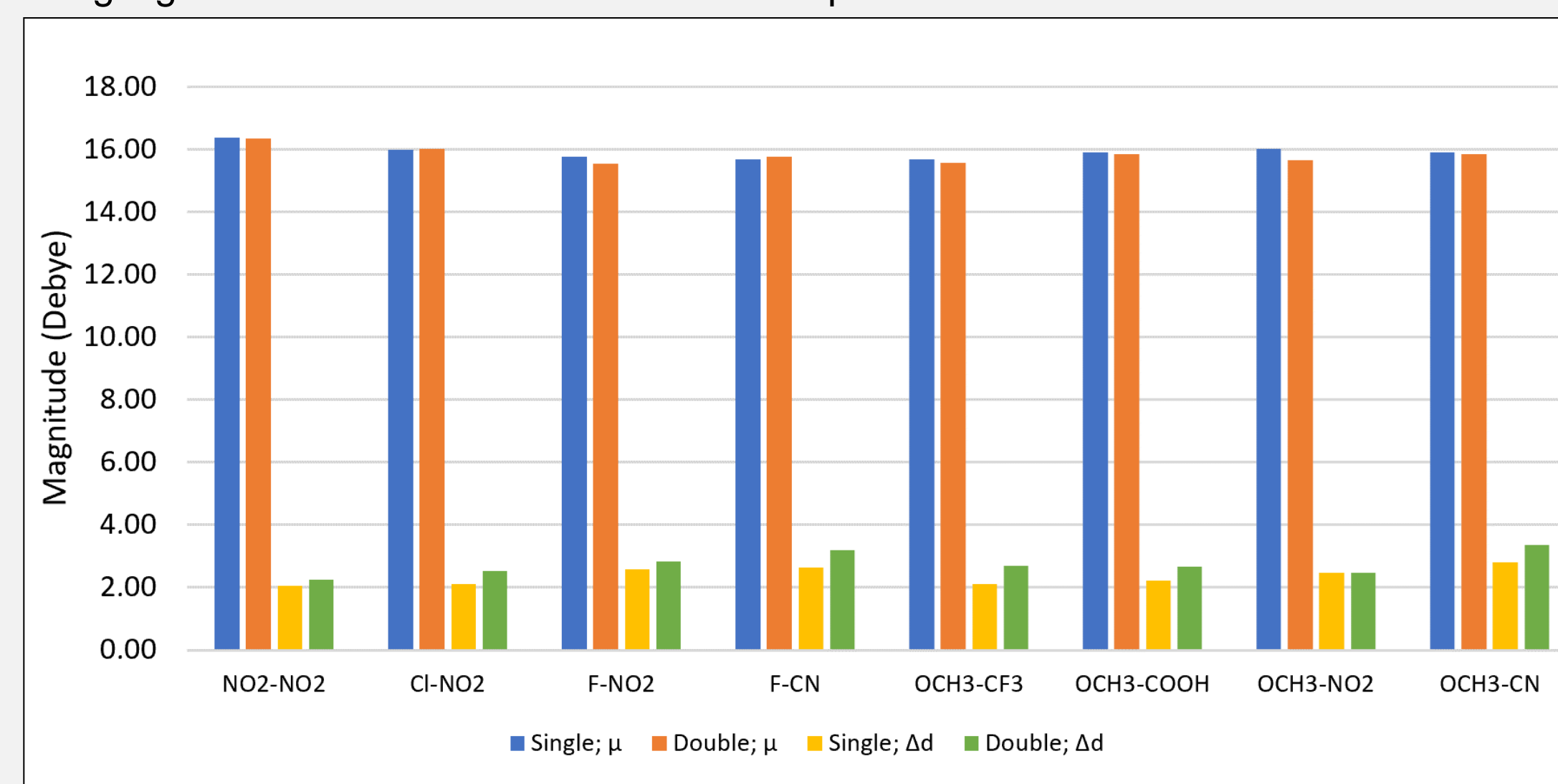


**Figure 4**. Magnitudes of transition dipole moments and static dipole differences for singly and doubly substituted Cy5 dyes. For double substitutions, two of the same substituent were added on the same side of the dye.

- Overall, D-D and D-W substituted dyes are less soluble than W-W substituted dyes (Fig. 2).
- Most soluble Cy5 is with SO₃H-SO₃H substituent pair (Fig. 2).
- Dyes in water exhibit less negative $\Delta G_{solv}$ (are less soluble) than in other solvents (Fig. 2).
- Substituents have minimal effect on $\mu$.
- Largest $\Delta d$ observed for W-W and D-W substituted dyes. Dyes with strong withdrawing substituents (e.g., NO₂ and CN) and either a weak withdrawing or a weak donating substituent produce largest $\Delta d$ (Fig. 3).
- Doubling the substituents slightly increases $\Delta d$; doubly substituted OCH₃-CN exhibited the largest $\Delta d$ (Fig. 4).

## 4. Results and Discussion, Part B
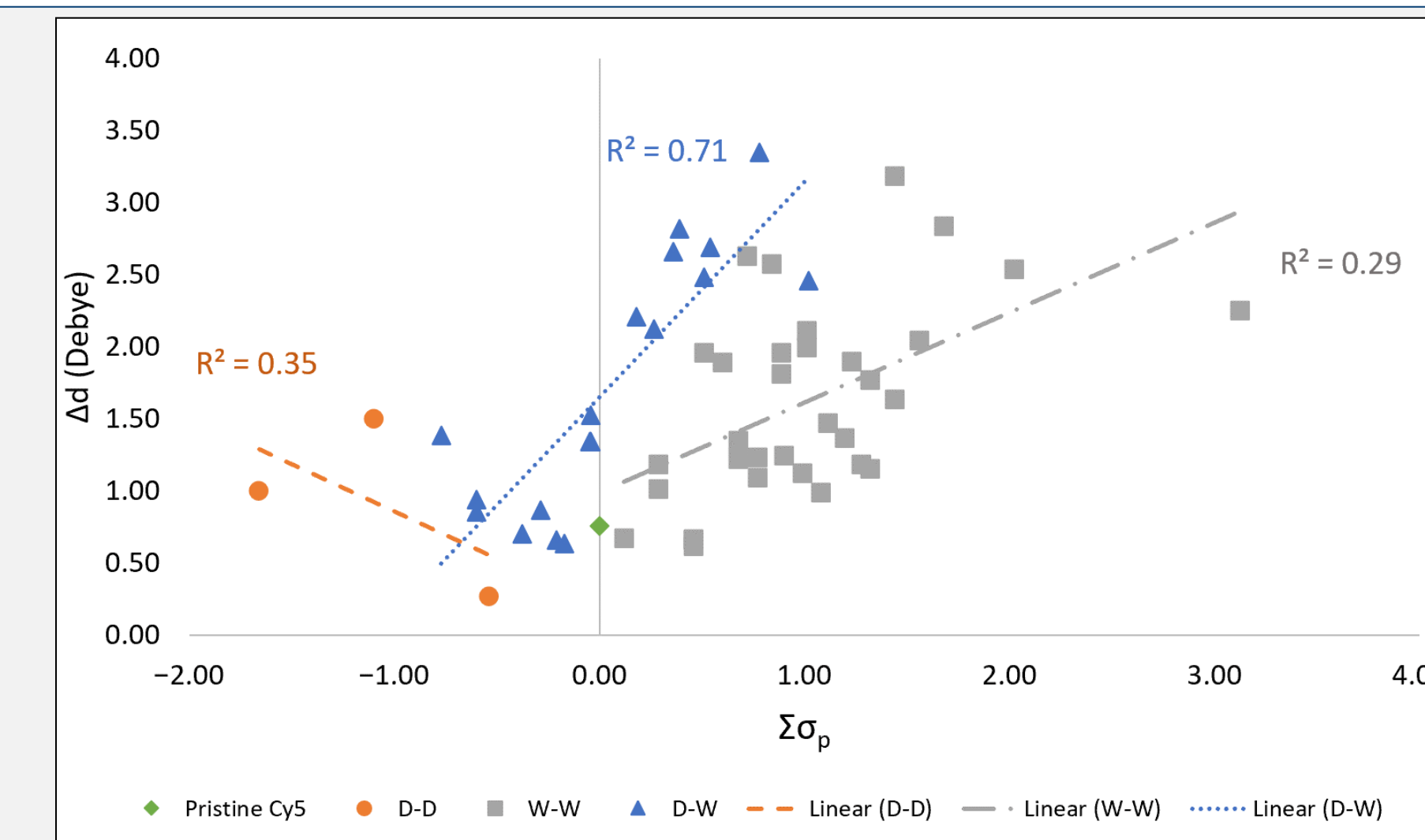


**Figure 5**. Static dipole difference magnitudes ($\Delta d$) plotted against the sum of Hammett constants ($\Sigma\sigma_p$) attached to the Cy5 dyes. Linear fits of the separate sets of data are shown along with corresponding $R^2$ values.

- Plotted $\Delta d$ versus the sum of the Hammett constants ($\Sigma\sigma_p$) and assumed a linear relationship for simplicity.
- Weak linear correlation for D-D and W-W pairs (Fig. 5).
- Stronger linear correlation for D-W pairs.
- In general, as $|\Sigma\sigma_p|$ increases, so does $\Delta d$. For W-W and D-W pairs, this implies a stronger dependence of $\Delta d$ on substituent withdrawing strength.

## 5. Conclusions

- We performed DFT and TD-DFT calculations to investigate the effects of substituent pairs attached to the ends of Cy5 on solubility and electronic properties
- Solvation energy ($\Delta G_{solv}$) and static dipole difference ($\Delta d$) were altered.
- W-W pairs were found to have the most negative $\Delta G_{solv}$ (more soluble), overall.
- More negative $\Delta G_{solv}$ in pyridine, quinoline, and isoquinoline compared with water indicates dye intercalation into DNA is favorable.
- Substituents have minimal effect on transition dipole moments ($\mu$)
- Up to a three times increase (compared with pristine Cy5) in $\Delta d$ facilitated by substituents, especially for W-W and D-W pairs such as F-CN and OCH₃-CN.
- Overall, an increase in the magnitude of the sum of Hammett constants ($|\Sigma\sigma_p|$) correlated to an increase in $\Delta d$.
- Stronger dependence of $\Delta d$ on substituent electron withdrawing strength.

## 6. References and Acknowledgments

**References**: **[1]** R. Monshower, *et al.* J. Phys. Chem. B 1997, 101, 7241; **[2]** J.M. Lim *et al.* Chem. Sci. 2013, 4, 388; **[3]** B.L. Cannon *et al.* J. Phys. Chem. A 2018, 121, 6905; **[4]** B.L. Cannon *et al.* J. Phys. Chem A 2018, 122, 2086; **[5]** D. Abramavicius *et al.* Chem. Phys. 2009, 357, 79; **[6]** A. Biaggne *et al.* Molecules 2021, 26, 524; **[7]** J. Fothergill *et al.* J. Phys. Chem. A 2018, 122, 8989; **[8]** D. Jacquemin. J. Chem. Theory Comput. 2016, 12, 3993; **[9]** C. Hansch *et al.* Chem. Rev. 1991, 91, 165; **[10]** Imaizumi *et al.* J. Radioanal. Nucl. Chem. 2002, 252, 467.