

Substituent effects on the thermodynamics parameters and emission energies of 2-amino-1,4-naphthoquinone derivatives

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Synopsis. The thermodynamics parameters revealed that methyl, fluorine and hydrogen substituents in the position R₃ of 2-amino-naphthoquinone (ANQ) derivatives were favorable. Fluorine substituents are highly electronegativity and increase the acidity of the amino group, promoting the ESIPT process. The PCA analysis from the emission energy values showed that electron donor groups at position R₃ or R₅, which promote red fluorescence, while withdrawing groups in the same position promoting a blue fluorescence. Our findings point out that substituents with higher electron density promote red-shifting wavelength. In fact, the substituent effects provide an understanding about behavior during the ESIPT process in ANQ derivatives, and how thermodynamic parameters can be influenced.

The ESIPT process is a fluorescent emission that involve an intramolecular proton transfer in the excited state from oxygen of the keto group to hydrogen atom of the amino group [1].

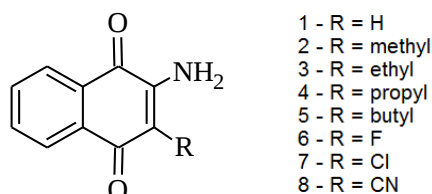


Figure 1. Chemical structure of 2-amino-1,4-naphthoquinone derivatives.

Eight from a group of thirty six ANQ derivatives are shown in figure 1. The geometry optimization was performed at the DFT/DGTVZVP /B3LYP and TDDFT/DGTVZVP/CAM-B3LYP levels [2]. The solvent effect was investigated with COSMO model. The thermodynamics parameters were carried out using IR calculations in ORCA program [3].

Table 1. Kinetic and thermodynamic parameters (kcal/mol) of the naphthoquinone derivatives.

	Kinetic				Thermodynamic	
	$\Delta G^\ddagger$	K	ΔG^{*}	k^*	ΔG	ΔG^*
1	37.54	6.07E+12	24.35	5.97E+12	11.82	-14.38
2	76.30	5.69E+12	58.99	5.63E+12	12.77	-18.92
3	66.99	5.78E+12	45.85	5.76E+12	11.75	6.31
4	68.83	5.76E+12	42.02	5.79E+12	10.72	0.31
5	79.85	5.67E+12	64.73	5.58E+12	11.87	11.83
6	39.85	6.05E+12	21.04	6.00E+12	13.96	-18.24
7	36.00	6.47E+12	19.00	6.49E+12	11.91	3.58
8	54.24	5.91E+12	17.98	6.03E+12	23.15	34.00

The thermodynamics parameters revealed that methyl (2), fluorine (6) and ANQ (1) were thermodynamic favorable in the excited state, according table 1. Compound 7 and 2 showed the highest and low-

est rate constant, respectively. In the excited state, compound 1, 6, 7 and 8 showed lower transition state Gibbs free energy values for the ESIPT process.

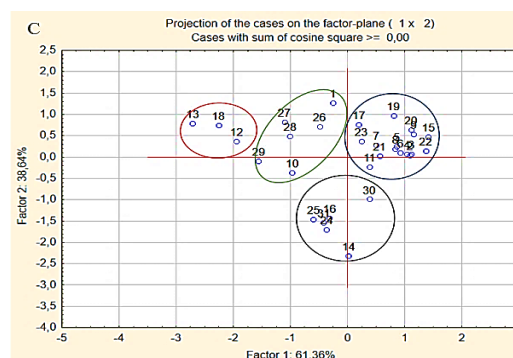


Figure 3. PCA graph for the emission energy values.

Figure 3 shows the PCA analysis for the emission energies of 36 ANQ derivatives. The first group, localized between 0 and 1 in Figure 3, which have electron withdrawing groups showed the blue fluorescence emission. Now, the group localized between 0 and -2 exhibited a fluorescent emission between blue and red. Finally, the group localized over -2 showed red fluorescence. This group was characterized with the presence of electron donor groups.

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References

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