

Molecular Design of New Organic Electroluminescence Materials: DCM Derivatives

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Abstract

We performed semiempirical (AM1 and ZINDO) and ab initio (HF and DFT) calculations, to investigate molecular structures and optical properties of DCM and its derivatives. DCM and its derivatives are used as a red fluorescent dopant of the organic electroluminescent host materials, Alq₃. We have studied the relationship between the molecular structure and the optical properties of these molecules for the improvement of EL efficiencies. Wavelength at the absorption maximum was found to be red-shifted when the molecule is substituted with both strong electron donating and withdrawing functional groups. A new red fluorescent dye was predicted by QSPR study based on calculations and experimental data.

1. Introduction

Quantum chemical studies have been performed to design a new light emitting organic materials. The energy states of molecules correspond to electronic, vibrational, rotational, and translational degree of freedom. The dominant energy transitions are electronic with energy spacing of few eV. Each electronic state corresponds to a bonding or anti-bonding molecular orbital. Since the optical properties of the molecules have direct relationship with electronic structures, the quantum chemical calculation methods have been applied for the investigation of structural variations and chemical environment of fluorescent molecules for a long time. We have studied the possibility of emission color tuning of EL materials

through control of conjugated π electrons. Stability and electro-optic transformation property of some Dicyano-Methylene-Pyran (DCM) derivatives [1,2], red dopant molecules have been investigated by semi-empirical and DFT methods. The calculation results were correlated with the experimental observations and a molecule with better optical property was predicted from the structure and property correlations.

2. Calculations

Semi-empirical AM1 and PM3 methods were used for structural optimization and then energies, dipole-moments, and polarizabilities of the molecules were calculated by ab-initio methods such as HF/6-31G* [3] and B3LYP/6-31G* [4]. The electronic transition was calculated by ZINDO [5] methods for the study of electronic transitions and optical properties of the luminescence molecules.

3. Results and discussion

The energy states of molecules are influenced by the molecular structure. Many virtual derivatives of DCM molecules were designed and their electronic energy states were calculated. DCJTB, one of the DCM derivatives are given in Figure 1 and its optimized structural parameters are summarized in Table 1.

Two important factors were considered for the design of new DCM derivatives. The first was an oscillation strength (OS), indicating a populations of electronic transition between the orbital energy levels and the second was proportionality between the position of absorption and emission bands. New

molecular structure were supposed from the calculation results of electronic structure, atomic charge, HOMO-LUMO gap, absorption band,

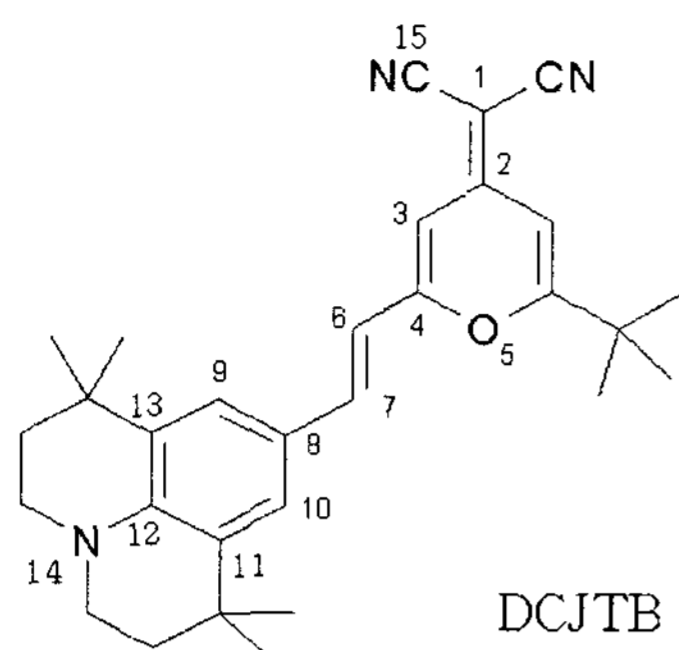


Figure 1. DCJTB, a DCM derivatives structure

Table 1. Geometry parameters of DCJTB using various methods.

Parameters	Methods			
	AM1	PM3	HF/ 6-31G*	B3LYP/ 6-31G*
Distance(Å)				
C1-C2	1.37	1.37	1.37	1.40
C3-C4	1.36	1.36	1.34	1.37
C4-C6	1.45	1.46	1.46	1.44
C6-C7	1.35	1.34	1.33	1.36
C7-C8	1.45	1.46	1.47	1.45
C12-N4	1.40	1.43	1.39	1.39
Angle(°)				
C3-C4-C6	124.2	122.9	123.8	124.4
C15-C1-C2	121.9	122.3	121.1	121.1
Dihedral angle(°)				
C6-C7-C8-C9	6.1	0.3	1.2	1.7
C3-C4-C6-C7	179.9	178.7	179.9	179.2
C9-C13-C12-N14	177.1	173.8	179.1	179.2

Experimentally measured dihedral angle C6-C7-C8-C9 was 11°.

oscillation strength (OS) and dipole moment of the molecules. The conjugation length from C1 to N14 and the functional groups substituted at phenyl ring or vinylene bridge between phenyl rings played a key role in determination of absorption peaks of the molecule. The electron donating groups cooperated with electron withdrawing CN group on pyran moiety and stabilized the HOMO level consequently raised the ionization potential of the molecule. The absorption bands were calculated to be in the range between 380 – 390 nm, mostly influenced by HOMO-LUMO gap and dipole moment. The calculated optical properties and OS are listed in Table 2.

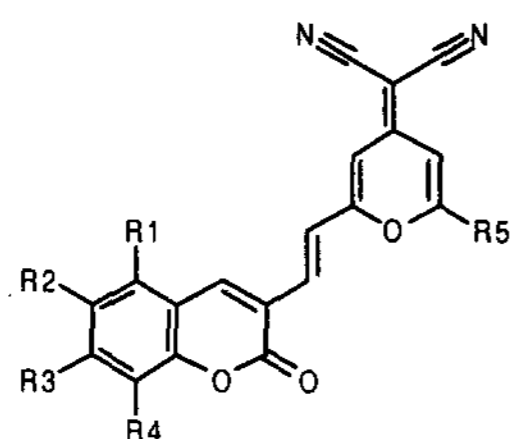
Table 2. Calculated absorption λ_{max} (nm) and oscillation strength of DCM derivatives.

Compounds	Gas Phase	
	AM1	B3LYP/6-31G*
DCM	375(1.563)	391(1.564)
DCMB	375(1.524)	391(1.545)
DCMM	373(1.501)	389(1.481)
DCJ	378(1.583)	393(1.567)
DCJT	376(1.565)	392(1.554)
DCJTB	376(1.520)	392(1.542)
DCJTE	376(1.542)	392(1.545)
DCJTM	374(1.499)	390(1.479)
DCJTT	376(1.526)	392(1.525)
DCJTP	376(1.528)	391(1.482)

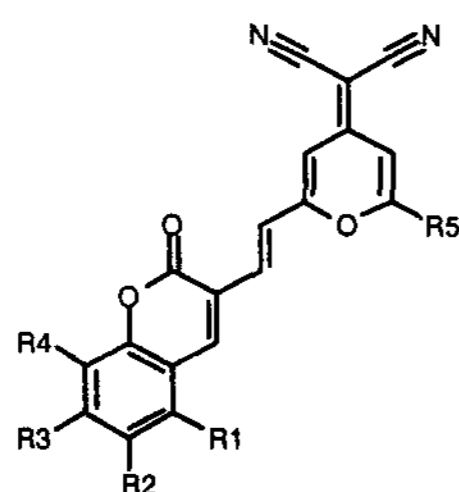
Meantime, electron donating group on pyran moiety destabilized the HOMO level compare to the one substituted with CN group. The electron populations of LUMO were dominant on pyran moiety whereas those of HOMO are dispersed all over the molecule along the conjugated bondings.

Some new molecular skeletons synthesized by coupling reaction of coumarine and pyran derivatives were designed through theoretical conformational studies. Structure **1** and **2** are favorable isomers among total four conformers. The structures based on these two isomers showed similar optical properties along with 30 % of oscillation strength improvement compare to the DCM derivatives. To predict a new dopant molecule, quantitative structure-property relationship (QSPR) [6] study was performed using quantum chemical calculation and statistical reg-

ression method. Newly predicted molecular structures showed about twice larger photoluminescence intensity compare to previously reported DCM derivatives.



1



2

Experimental measurements and the predicted photoluminescence values were correlated in Figure 2 (right) and important descriptors in the regression

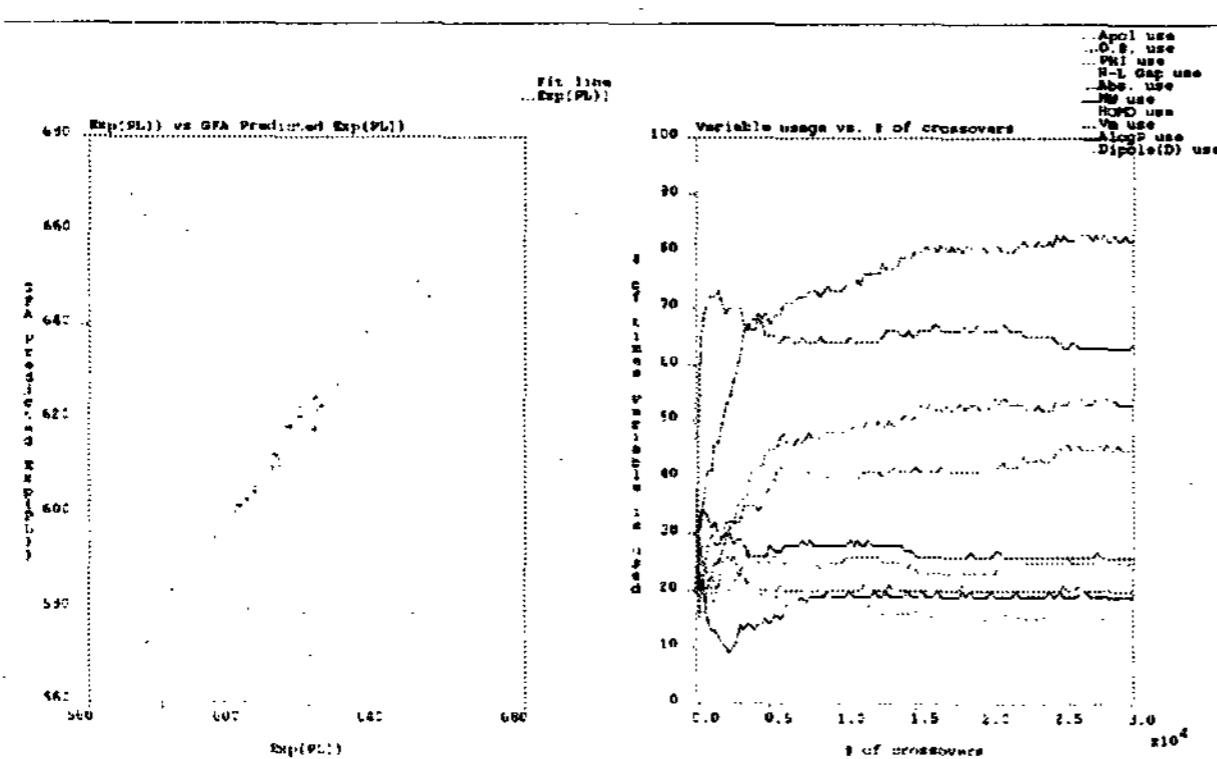


Figure 2. Multiple linear regression by genetic algorithm.

equation are indicated in the order of usefulness in left of Figure 2. The selected fitting equation using GFA method has been given as following

$$\text{Exp (PL)} = 3408.58 - 2.56953 \times (\text{Abs}) - 266.828 \times (\text{H-}$$

$$\text{L Gap}) - 12.5873 \times (\text{PHI}) + 0.006514 \times (\text{Apol})$$

The equation consists of four descriptors such as absorption wavelength, HOMO-LUMO gap, molecular flexibility, and atomic polarization. The regression result showed R^2 value of 0.87.

4. Conclusion

Theoretical methods, combined with experimental data gave reliable results for the prediction of photoluminescence of the dopant molecules. The molecular structure calculated quantum mechanical calculations and statistical methods showed good correlation with experimental observations. The newly designed coumarin-pyran coupled molecule, SSSH3 showed 2.2 times larger efficiency compare to that of DCM. The absorption λ_{max} was observed on 510 nm in red color region. These approaches are found to be very useful for synthetic design and the development of new organic EL materials.

5. Acknowledgements

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6. References

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