Article

Anthracene chromophore와 diphenyl amine 유도체로 구성된 유기발광재료에 관한 광학실험과 전자구조계산의 비교

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Comparison of Experimental Results and Electron Structure Calculations on Organic Light Emitting Materials Consisting of an Anthracene Chromophore and Diphenyl Amines Derivatives

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초 록

유기발광 다이오드 발광재료를 r^2SCAN-3c, B3LYP/def2-TZVP, DLPNO-STEOM-CCSD/def2-SVP와 같은 세 가지 전자구조계산 방법들을 이용한 전자구조 계산을 통해 구조최적화, 분자궤도 함수, excitation을 예측하였다. 또한, 계산 방법에 따른 차이를 알아보고 실험값과 비교를 통해 적합한 계산 방법을 찾아내는 연구를 진행하였다. 선정된 5개의 발광재료들은 anthracene chromophore에 diphenyl amine이 치환된 N,N,N',N'-tetraphenyl-anthracene-9,10-diamine (TAD)를 포함하여 위치와 크기를 달리한 alkyl group들이 치환되어 있다. 계산에 의한 정성적 예상은 실험결과와 대부분 일치하였으며, 이 중 B3LYP/def2-TZVP 방법의 결과가 실험결과와 absorption wavelength 면에서 가장 오차가 적었으며, 적합한 계산 방법으로 확인되었다.

Abstract

The electronic structure calculations for organic light-emitting diode-emitting materials were performed using three different methods: r^2SCAN-3c, B3LYP-D3/def2-TZVP, and DLPNO-STEOM-CCSD/def2-SVP. These calculations were used to predict structure optimization, molecular orbitals, and excitation properties. Additionally, the differences among the calculation methods were investigated and compared with experimental values to identify the most suitable computational method. The five selected emitting materials include N,N,N',N'-tetraphenyl-anthracene-9,10-diamine, in which diphenyl amines are substituted on an anthracene chromophore, along with other alkyl groups of varying sizes and positions. The qualitative predictions made by the calculations were mostly consistent with the experimental results, and among them, the B3LYP/def2-TZVP method showed the smallest error in absorption wavelength compared to the experimental results, confirming it as the most suitable calculation method.

Keywords: Electron structure calculations, Geometry optimization, OLED, Anthracene, Diphenylamine

1. Introduction

Various electronic structure calculation methods based on quantum mechanics have competitively evolved by incorporating multiple theories and approximations. Among them, the most widely used is density functional theory (DFT), a type of single-reference self-consistent field (SCF) methods. DFT calculations involve selecting a pair of combinations from hundreds of available functionals and basis sets. The level of functionals and basis sets is classified based on the type of additional functions and the number of parameters, which determines the accuracy and scalability of the calculations. The reason for proposing so many functionals and basis sets is that a universal combination capable of accurately calculating all molecules at the same level has yet to be found. Fundamentally, DFT is useful for determining optimized molecular structures through energy calculations and predicting the resulting properties of materials. It can also aid in understanding electron

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levels and states by classifying molecular orbitals. In addition to DFT, there are methods such as single-reference correlation, multi-reference SCF, and local correlation methods (e.g., domain-based local pair natural orbital-coupled cluster singles and doubles (DLPNO-CCSD)), which improve accuracy but require relatively more computational resources compared to DFT. Electronic structure calculation methods are utilized not only for structure optimization but also for interpreting various properties of materials, such as thermodynamic analysis through vibrational frequency calculations, reaction energy, and excitation properties. Particularly, excited states can be calculated using methods like time-dependent DFT (TD-DFT), the equation of motion (EOM) CCSD, and the similarity transformed EOM (STEOM) CCSD. These methods allow for the analysis of the energy of the wavelength absorbed by light corresponding to specific singlet or triplet excitations, as well as the interpretation of oscillator strength and spin-orbit coupling.

Over the past few decades, research has advanced the development of blue-emitting materials with improved stability and efficiency using various experimental methods and the aforementioned electronic structure calculation techniques. Electronic structure calculations, in particular, offer advantages such as guiding development directions and reducing development costs. When designing molecular structures for organic semiconductors or OLEDs, these calculations can help predict material properties and select materials that meet specific requirements for initial application. They also facilitate the creation of optimized devices and aid in device analysis. In this study, we compared and analyzed the correlation between molecular structure changes and optical properties by introducing alkyl groups into diphenyl amine on an anthracene core with experimental and computational methods. Among the three calculation methods used in this paper, r²SCAN-3c is a method introduced in 2021 and is known to be faster and more accurate than previously used methods[1,2]. It was selected to verify whether it accurately calculates excitation as well. Additionally, B3LYP/def2-TZVP is one of the most widely used functional/basis set combinations in DFT, while DLPNO-STEOM-CCSD is a high-level calculation method known for its accuracy in excitation calculations, though it requires significant time and computational resources. Therefore, def2-SVP, a lower-level basis set, was used with this method to determine whether accurate results could still be obtained while reducing computation time.

2. Experiments and calculations

2.1. Materials

The five substances studied in this research are selected from those that are already reported, and have the molecular structures shown in Figure 1: N,N,N',N'-tetraphenyl-anthracene-9,10-diamine (TAD)[3], N,N,N',N'-tetra-o-tolyl-anthracene-9,10-diamine (o-Me-TAD)[4], N,N,N',N'-tetra-m-tolyl-anthracene-9,10-diamine (m-Me-TAD)[3], N,N,N',N'-tetra-p-tolyl-anthracene-9,10-diamine (p-Me-TAD)[3], and N⁹,N¹⁰-bis(5-(tert-butyl)-2-methylphenyl)-N⁹,N¹⁰-bis(2,4-dimethylphenyl)anthracene-9,10-diamine (3Me-1Bu-TPADA)[5]. In these materials, TAD consists of anthracene with diphenyl amine substituted. In o-Me-TAD, m-Me-TAD, and p-Me-TAD, a methyl group is introduced at the ortho, meta, and
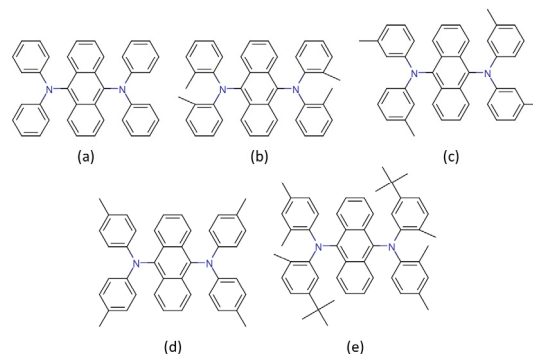
Figure 1. The molecular structures of the anthracene-core compounds. (a) TAD, (b) o-Me-TAD, (c) m-Me-TAD, (d) p-Me-TAD, and (e) 3Me-1Bu-TPADA.

para positions relative to the nitrogen in TAD, respectively. In 3Me-1Bu-TPADA, methyl groups are introduced at the ortho and para positions, while a tert-butyl group is introduced at the meta position.

2.2. Electronic structure calculations

In this study, we used the software package ORCA for electronic structure calculations[6]. Two different methods were employed for the structural optimization of the five molecules. First, r²SCAN-3c is a composite electronic structure calculation method that uses the meta-generalized-gradient approximation (mGGA) functional with the mTZVPP basis set. It is known to perform relatively accurate structure and energy calculations quickly using density functional theory (DFT)[5]. The B3LYP-D3/def2-TZVP method, one of the most widely used DFT functional/basis set pairs, is considered to have a moderate level of accuracy in structure optimization and energy calculations[7,8]. We also calculated the molecular orbital (MO) levels using these two methods.

We further analyzed electron excitation using configuration interaction with singles (CIS) for r²SCAN-3c and time-dependent density functional theory (TDDFT) calculations for B3LYP-D3/def2-TZVP. Additionally, we calculated the excitation energy by applying the domain-based local pair natural orbital similarity transformed equation of motion-coupled cluster singles and doubles (DLPNO-STEOM-CCSD) method with the def2-SVP basis set to the B3LYP-D3/def2-TZVP optimized structures[8,9]. This method is expected to provide relatively very small errors in excitation energy calculations.

3. Results and discussion

3.1. Experiments for molecular structures and photophysical properties

The anthracene chromophore is planar, allowing for easy intermolecular packing, which can lead to crystal formation in thin films, making it unsuitable as a material for organic light-emitting diodes (OLEDs) on its own. Therefore, substituents that can suppress intermolecular interactions and maintain an appropriate distance between molecules need to be introduced. The closer the dihedral angle formed

Table 1. Measured Wavelengths for Absorption and PL_max of the Anthracene Core Molecules

Materials	Solution (in toluene)			Film (evaporated film, 50 nm)		
	λ a_abs (nm)	PL_max (nm)	FWHM (nm)	λ abs (nm)	PL_max (nm)	FWHM (nm)
TAD	458	508	57	468	518	61
o-Me-TAD	470	518	56	477	528	58
m-Me-TAD	465	517	56	472	526	59
p-Me-TAD	476	529	56	480	534	58
3Me-1Bu-TPADA	487	528	55	485	531	55

between the substituted side group and the anthracene is to 90°, the more steric hindrance it causes, and the bulkier the substituent, the more it reduces strong π-π interactions that induce packing. Such molecules can remain amorphous in thin-film form or, depending on the type of side group, induce horizontal orientation, leading to high efficiency when applied as an emissive layer (EML). The side groups used in this study are based on diphenyl amine, and the photophysical properties were measured depending on the presence and position of alkyl groups, then compared with the results of electronic structure calculations (Table 1).

According to the experiment, these molecules exhibited an absorption range of approximately 300~500 nm in solution. The absorption peak between 320~400 nm is due to the π-π* transition of anthracene, while the absorption around 400~500 nm is attributed to intra charge transfer between anthracene and diphenyl amine. The photoluminescence (PL) maximum wavelength was observed between 508~528 nm, corresponding to emission in the green region. The methyl-substituted o-Me-TAD, m-Me-TAD, and p-Me-TAD molecules showed emission in a red-shifted region compared to TAD. In particular, 3Me-1Bu-TPADA, due to the extended conjugation caused by the substituted alkyl groups, exhibited the longest emission wavelength at 528 nm. The trend in the film state was similar to that in the solution state, but the absorption and emission regions were red-shifted compared to those in the solution state.

3.2. Prediction of molecular geometry by calculations

The dihedral angles between the anthracene and diphenyl amine in TAD were 72.1° and 70.6°, and in the other four materials, they were similarly between 65.7° and 73.1° (Figure 2). Although alkyl groups were introduced to increase steric hindrance in the diphenyl amine unit, their small size likely had little effect on the dihedral angles. However, when examining the full width at half maximum (FWHM) of the PL emission in solution, all five materials showed similar values of 55~57 nm. In the film state, TAD exhibited a broader FWHM of 61 nm, whereas the four alkyl-substituted materials showed slightly narrower FWHMs of 55~58 nm. Notably, 3Me-1Bu-TPADA demonstrated the narrowest PL emission at 55 nm, effectively suppressing molecular packing due to the introduction of various alkyl groups. These results suggest that the introduced methyl and butyl groups effectively sup-
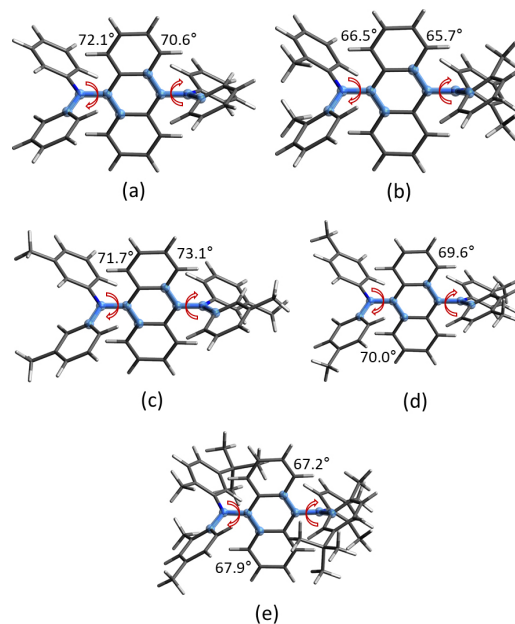
Figure 2. Dihedral angles of compounds geometrically optimized by B3LYP-D3/def2-TZVP DFT calculations. (a) TAD, (b) o-Me-TAD, (c) m-Me-TAD, (d) p-Me-TAD, and (e) 3Me-1Bu-TPADA.
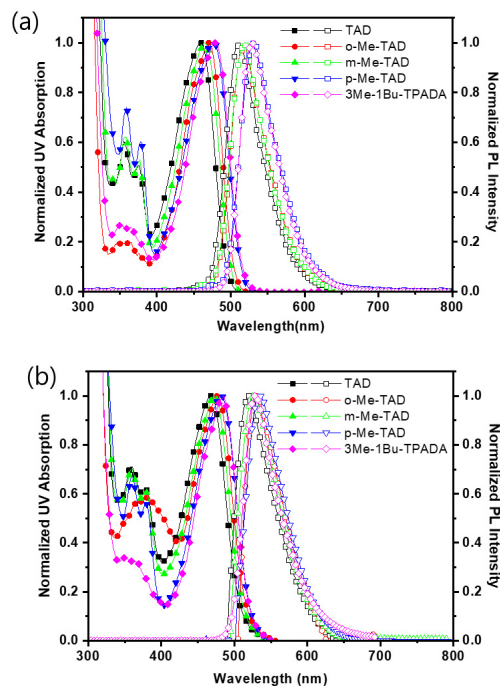
Figure 3. UV-Vis absorption and PL spectra of the materials in toluene (a) and in film (b).

press intermolecular interactions (Figure 3 and Table 1).

3.3. Molecular orbitals

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), as well as the difference between

these two values, known as the HOMO-LUMO gap, significantly impact the characteristics of semiconductor materials and the design of organic light-emitting diode devices.

Molecular orbitals are related to the energy band gap of semiconductor materials, which has garnered significant interest in predictions made through calculations. However, in electronic structure calculations, molecular orbitals are described using a basis set. The parameters of this basis set are fitted to best describe the structure and formation energies of known molecular structures, making it challenging to obtain accurate energy levels for electronic orbitals using these basis sets. Despite this, understanding the structure of each molecular orbital and comparing their energy levels relatively remains useful for predicting trends in the HOMO-LUMO gap changes due to structural modifications during molecular design.

Figure 4 shows the molecular orbitals HOMO-1, HOMO, LUMO, and LUMO+1 for the five molecules. For all the molecules, the HOMO exhibits electron density distributed across the entire molecule due to the electron-donating effect of the side groups, while the LUMO is primarily distributed over the anthracene. This suggests that the introduced methyl groups have little effect on the overall electron density of the molecule. However, since the length of conjugation varies depending on the substitution position, the PL wavelength can change. In fact, experimental results confirm that the PL shifts to longer wavelengths in the order TAD < o-Me-TAD < m-Me-TAD < p-Me-TAD in both solution and film states.
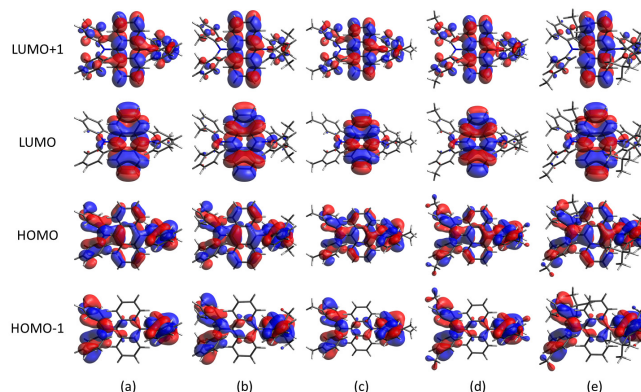
Figure 4. Molecular orbitals of TAD and its derivatives. (a) TAD, (b) o-Me-TAD, (c) m-Me-TAD, (d) p-Me-TAD, and (e) 3Me-1Bu-TPADA.

Table 2 compares the experimental HOMO-LUMO values of each compound with the results from various electronic structure calculations. The r^2SCAN-3c calculations generally yield a lower LUMO and a higher HOMO, leading to an underestimated HOMO-LUMO gap. In contrast, the DLPNO-STEOM-CCSD/def2-SVP calculations tend to predict a higher LUMO and a lower HOMO compared to the experimental values. Although this method requires substantial computational resources due to its high level of accuracy, it does not accurately describe the energy levels of the molecular orbitals. While not entirely accurate, the B3LYP-D3/def2-TZVP calculations—one of the most

Table 2. HOMO/LUMO Energy Levels of the Compounds

Molecule	Method	LUMO (eV)	HOMO (eV)	HOMO-LUMO gap (eV)
TAD	Experiment[a]	-3.050	-5.570	2.520
	r2SCAN-3c	-2.737	-4.614	1.877
	B3LYP/def2-TZVP	-2.246	-5.181	2.935
	DLPNO-STEOM-CCSD/def2-SVP	1.178	-6.867	8.045
o-Me-TAD	Experiment	-2.950	-5.400	2.450
	r2SCAN-3c	-2.644	-4.516	1.872
	B3LYP/def2-TZVP	-2.161	-5.078	2.917
	DLPNO-STEOM-CCSD/def2-SVP	1.260	-6.684	7.944
m-Me-TAD	Experiment	-2.980	-5.450	2.470
	r2SCAN-3c	-2.633	-4.487	1.854
	B3LYP/def2-TZVP	-2.163	-5.080	2.917
	DLPNO-STEOM-CCSD/def2-SVP	1.262	-6.792	8.054
p-Me-TAD	Experiment	-2.990	-5.390	2.400
	r2SCAN-3c	-2.607	-4.383	1.776
	B3LYP/def2-TZVP	-2.130	-4.963	2.833
	DLPNO-STEOM-CCSD/def2-SVP	1.268	-6.739	8.007
3Me-1Bu-TPADA	Experiment	-3.110	-5.500	2.390
	r2SCAN-3c	-2.587	-4.387	1.800
	B3LYP/def2-TZVP	-2.113	-4.958	2.845
	DLPNO-STEOM-CCSD/def2-SVP	1.337	-6.448	7.784

[a] HOMO was measured by AC-2, the HOMO-LUMO gap was obtained from the absorption spectrum edge in the solution state, and the LUMO was defined by the HOMO and the HOMO-LUMO gap.

Table 3. Calculation Results for the Excitations of the Compounds

Compound	Method	Absorption		Oscillator strength	Characteristic of transition	Contribution (%)
		(nm)	(eV)			
TAD	r^{2}SCAN-3c	597.4	2.075	0.120	H→L	89.6
	B3LYP/def2-TZVP	511.1	2.426	0.139	H→L	90.9
	DLPNO-STEOM-CCSD/def2-SVP	407.3	3.044	0.277	H→L	74.6
	Experiment (in film)	468	2.650			
o-Me-TAD	r^{2}SCAN-3c	568.2	2.182	0.166	H→L	86.4
	B3LYP/def2-TZVP	497.7	2.491	0.201	H→L	89.9
	DLPNO-STEOM-CCSD/def2-SVP	410.0	3.024	0.389	H→L	81.6
	Experiment (in film)	477	2.600			
m-Me-TAD	r^{2}SCAN-3c	604.2	2.052	0.128	H→L	90.3
	B3LYP/def2-TZVP	517.8	2.394	0.137	H→L	91.7
	DLPNO-STEOM-CCSD/def2-SVP	396.5	3.127	0.296	H→L	77.8
	Experiment (in film)	472	2.627			
p-Me-TAD	r^{2}SCAN-3c	634.1	1.955	0.126	H→L	92.3
	B3LYP/def2-TZVP	537.0	2.309	0.125	H→L	93.5
	DLPNO-STEOM-CCSD/def2-SVP	400.5	3.096	0.299	H→L	81.4
	Experiment (in film)	480	2.583			
3Me-1Bu-TPADA	r^{2}SCAN-3c	605.5	2.048	0.194	H→L	89.1
	B3LYP/def2-TZVP	529.1	2.343	0.227	H→L	92.2
	DLPNO-STEOM-CCSD/def2-SVP	440.7	2.813	0.390	H→L	84.7
	Experiment (in film)	485	2.557			

commonly used DFT levels—provided results for excited states that were closest to the experimental values. These results indicated that the relationship of HOMO-LUMO gaps follows the order: TAD > o-Me-TAD, m-Me-TAD > p-Me-TAD, 3Me-1Bu-TPADA, which is similar to the trend observed in the experimental band gaps.

3.4. Excitation

In the development of organic light-emitting diodes (OLEDs), the most crucial characteristic is the electroluminescence (EL) wavelength, which determines the emission color. However, directly obtaining this value from electronic structure calculations is challenging. Instead, the wavelengths at which organic light-emitting molecules absorb light can be calculated using TDDFT or CIS methods. According to Table 3, the predicted trends are similar to those observed in the HOMO-LUMO gap results. The r^{2}SCAN-3c and B3LYP/def2-TZVP calculations predicted longer wavelengths compared to the experimental measurements, while the DLPNO-STEOM-CCSD/def2-SVP calculations predicted shorter absorption wavelengths. Among these, the B3LYP/def2-TZVP results were the closest to the experimental values. Analysis of the transition characteristics from the calculations suggests that most of the absorption is due to electron transitions from the HOMO to the LUMO levels. The oscillator strength in the calculations, which relates to the magnitude of the absorption peak, is predicted to increase with the introduction of side groups to TAD, making it advantageous for light absorption and emission.

4. Conclusion

We compared the optical properties measured experimentally with the predicted results from electronic structure calculations for five materials, each with different positions and types of alkyl groups introduced to anthracene and diphenyl amine. Analysis of the predicted molecular structures revealed that the introduced alkyl groups had little impact on the dihedral angle between anthracene and diphenyl amine, but did influence the PL characteristics depending on the position and size of the substituents. The band-gap measured experimentally closely matched the trend of the HOMO-LUMO gap predicted by the molecular calculations. Among the excitation calculations, the B3LYP-D3/def2-TZVP method provided results closest to the actual values. However, there are still significant discrepancies in accurately predicting absorption and emission colors. Current methods that yield results close to experimental values require substantial computational resources, indicating a need for further development of electronic structure calculation methods and useful strategies for accurate quantitative predictions.

Acknowledgments

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