

Theoretical Investigation of Pyrazolo[3,4-b]quinoline Derivatives as Emitting Materials

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Abstract

Recently, the Pyrazolo[3,4-b]quinoline (PAQ) derivatives were used as a dopant in the multiplayer OLED fabrication. The semiempirical AM1, ZINDO and ab initio DFT B3LYP calculation methods were used to calculate the maximum excitation wavelength (λ_{\max}^{ads}) and fluorescence wavelengths (λ_{emi}) of a series of PAQ derivatives based on their optimized structures. The substitution effects of PAQ derivatives with electron-withdrawing and electron-donating substituents were investigated according to their photo-physical properties and electroluminescent behavior. The calculated DT/DFT/B3LYP/6-31G* had the better linear relationship of them. Presumably, the procedures of theoretical calculation would be employed to predict the electroluminescence characteristics of the other material, and could give a possible way to design novel material for OLED.

Key Words: PAQ, DFT, OLED, Excitation

1. Introduction

Recently, the research in the organic light-emitting diodes (OLEDs) has become one of the most interesting topics in field of chemistry, physics and material science [1–7]. Since the initial works have been done on the small molecule by Tang et al. [8] and on the polymers by Friend et al. [9], lots of organic compounds were synthesized and applied to the OLED devices for the commercial applications. The organic compound contains pyrazoline moiety, which have been explored for the emitting layer and hole transporting material in the OLEDs [10,11]. Huang et al. proposed the pyrazoline derivatives, which could be used in OLED as emitting material [12–17]. Tao et al. used the diprazolopyridine derivatives as efficient blue light-emitting material in

multilayer OLED [18,19]. They also reported that diethylamino-substituted pyrazoloquinoline could generate a sharp green electroluminescence [20]. He et al. have studied the photo-physical properties of pyrazolo[3,4-b]quinoline (PAQ) derivatives, which could be the dopants in the polymer-LED materials [21]. In general, the characteristics of PAQ derivatives have the fluorescence wavelengths (λ_{emi}) in blue and bluish-green region. 1-Methyl-3-phenyl-1H-pyrazolo[3,4-b]quinolines (PAQ derivatives) carry different substituents have been synthesized by Tao's group as emitting material (Figure 1) [22]. According to the experimental data, the blue emission have been achieved with these PAQ derivatives as the dopant, in a device of structure:ITO/NPB/CBP/TPBI:PAQ-X/TPBI/Mg:Ag, where the PAQ-X is 1-methyl-3-phenyl-1H-pyrazolo[3,4-b]quinoline carrying various substituents, CBP is 4,4'-bis[N-(1-naphthyl)-N-phenylamino] biphenyl (α -NPB) and 4,4'-dicarbazolyl-1,1'-biphenyl as hole-

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transporting materials and TPBI is 2,2',2''-(1,3,5-phenylene)-tris[1-phenyl-1H-benzimidazole] as electron transporting material. Recently, Nizioł et al. proposed the optical properties of a series of PAQ derivatives [23]. They indicated that these PAQ derivatives have high quantum efficiency of emission in the blue and the green region.

At present, number of papers have been proposed in the theoretical investigation of OLED material using different calculation methods and generating their electronic and geometric structures, absorption and emission spectra [24–27]. Wang et al. used the semi-empirical AM1 and ab initio DFT methods to determine the electronic transition energies and relative intensities (oscillator strengths) for 1,4-distyrylbenzene (DSB) [28], pyrene and their derivatives [29]. Kościelniak et al. presented the experimental data and the semiempirical PM3 and AM1 calculations for the PAQ derivatives [30]. The comparison of measured and calculated absorption spectra by semiempirical AM1 method manifested rather good agreement for the PAQ derivatives, with three substituted radicals R_1 , R_2 , R_3 = methyl or phenyl groups (Figure 1) [30]. In the present work, the ab initio DFT B3LYP and the semiempirical AM1 methods were used for generating the geometrical and electronic structures, electronic transition energies (excitation and fluorescence) and relative intensities (oscillator strengths, f) for PAQ and its derivatives. Then, the calculated energies were calibrated based on the experimental data for these derivatives. The substituents and substitution position effects in PAQ derivatives were also investigated. In particular, the substitution position can be in five positions of the PAQ (Figure 1). The quantum chemistry calculations can

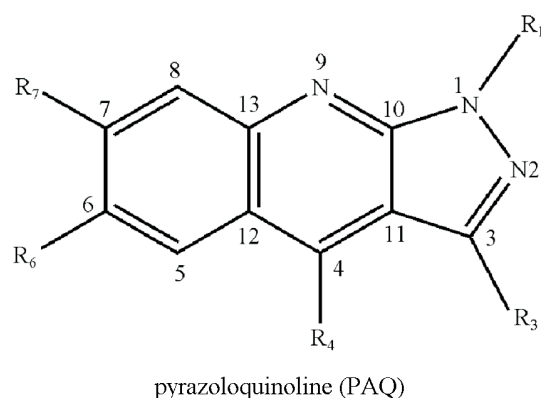


Figure 1. Five substitution positions of PAQ.

be used as a model system for understanding the relationship between luminescence and molecular structure for these PAQ derivatives.

2. Computations

In this work, ab initio DFT B3LYP, TD-DFT with 6-31G* basis set and the semiempirical AM1 and PM3 methods were used to generate the optimized structures of PAQ and its derivatives. Comparing the calculated results, the calculated geometrical parameters of PAQ (Table 1) by ab initio RHF/6-31G* and DFT B3LYP/6-31G* calculations have the similar results with those of the semiempirical AM1 and PM3 calculations. Due to the computing time limitation, the optimized structures of PAQ derivatives were determined by using the semiempirical AM1 and ab initio DFT B3LYP methods for this calculation. The electronic transition properties, which include the maximum excitation wavelength (λ_{\max}^{ads}) and relative intensities (oscillator strengths, f), were obtained by the semiempirical ZINDO method and time-dependent density functional theory (TD-DFT), respectively. These calculations were based on the optimized structures by DFT and AM1 methods and referred as “TD-DFT/method” or “ZINDO/method”. Where “method” was the level of geometry optimization. The keyword “EXICTED” was used for the optimized structure of the excited state (S_1). The fluorescence wavelengths (λ_{emi})

Table 1. Calculated bond lengths (Å) of optimized PAQ*

| Bond length | HF/6-31G* | B3LYP/6-31G* | AM1 | PM3 |
|-------------|-----------|--------------|-------|-------|
| N1-N2 | 1.350 | 1.360 | 1.330 | 1.370 |
| N2-C3 | 1.280 | 1.310 | 1.340 | 1.330 |
| C3-C11 | 1.440 | 1.430 | 1.460 | 1.440 |
| C11-C4 | 1.360 | 1.380 | 1.360 | 1.370 |
| C4-C12 | 1.400 | 1.410 | 1.410 | 1.410 |
| C12-C5 | 1.420 | 1.420 | 1.420 | 1.420 |
| C5-C6 | 1.350 | 1.370 | 1.360 | 1.360 |
| C6-C7 | 1.420 | 1.420 | 1.410 | 1.420 |
| C7-C8 | 1.350 | 1.370 | 1.360 | 1.360 |
| C8-C13 | 1.420 | 1.420 | 1.440 | 1.430 |
| N9-C13 | 1.340 | 1.350 | 1.370 | 1.370 |
| N9-C10 | 1.300 | 1.319 | 1.339 | 1.345 |
| C10-N1 | 1.350 | 1.360 | 1.410 | 1.400 |
| C10-C11 | 1.417 | 1.435 | 1.477 | 1.441 |
| C12-C13 | 1.420 | 1.440 | 1.438 | 1.420 |

* The molecular structure of PAQ is described in Figure 1.

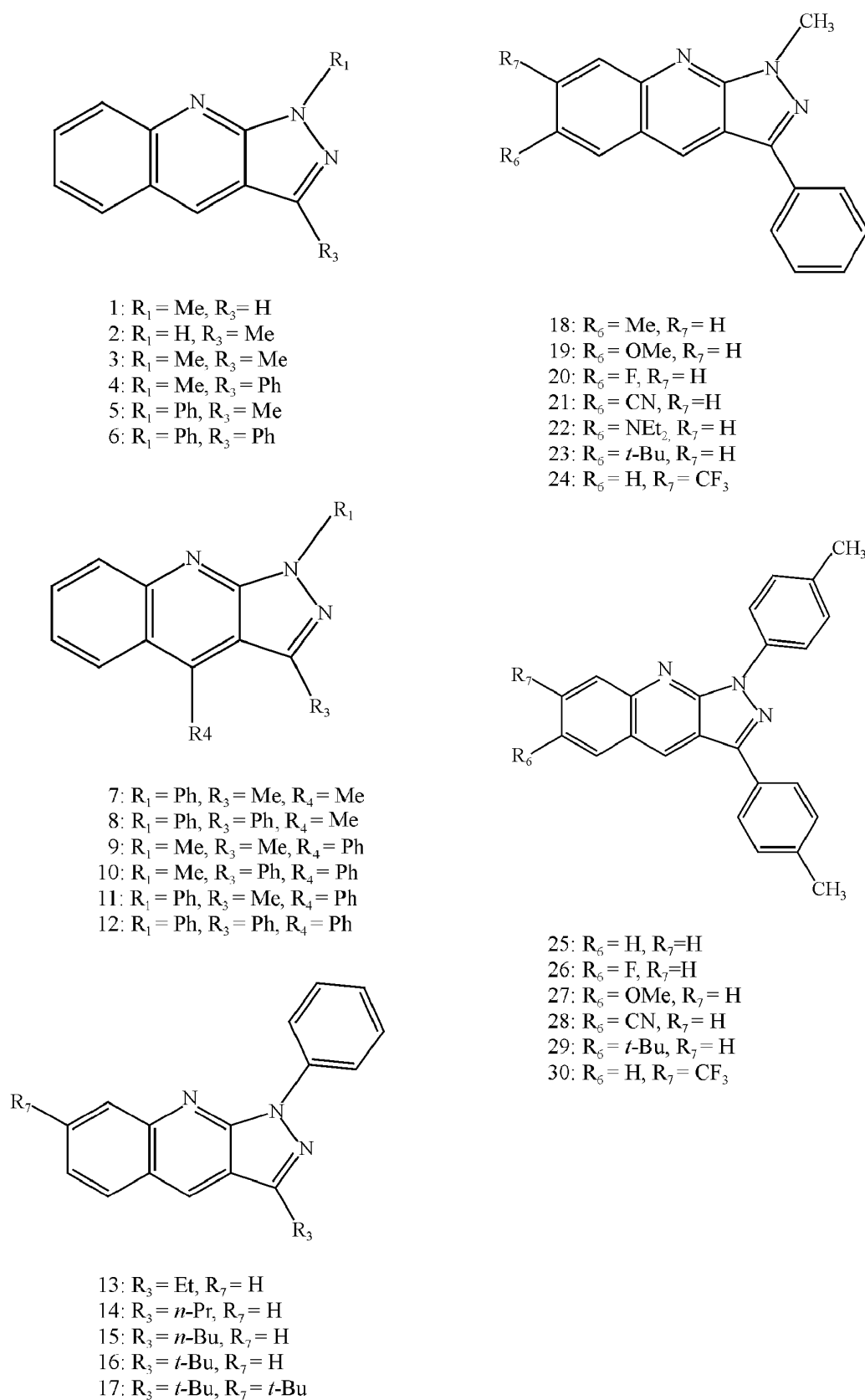


Figure 2. Molecular structures of PAQ derivatives.

and relative intensities (oscillator strengths, f) were determined by ZINDO calculations based on the optimized excited state structure, which was obtained from the AM1 calculation, we denoted as ZINDO/AM1 for this calculation. In this study, the vertical excited upward transition from the optimized structure in the excited state (S_j) equals the downward vertical fluorescence transition ($S_0 \leftarrow S_j$). The excitation energy calculations in this paper were limited to the first excited electronic state corresponding to the HOMO-LUMO single excitation. The semiempirical ZINDO, AM1, and ab initio DFT and TD-DFT calculations were performed employing the MOPAC 2000 [31] and Gaussian 03 packages [32], respectively. In this study, thirty PAQ derivatives in Figure 2 were investigated by the semiempirical AM1 method and ab initio DFT B3LYP method with 6-31G* basis set for the optimized structure and spectral properties.

3. Result and Discussion

3.1 Calculated Maximum Excitation Wavelength of PAQ and Its Derivatives

The molecular structures of PAQ and its derivatives were shown in Figure 2. In order to study the substituents effect in mono-substituted PAQ compound, difference substituents were added with five substitution positions of PAQ (Figure 1). Since these related PAQ derivatives have been proposed by the experimental work.

Calculated maximum excitation wavelength (λ_{\max}^{ads}) and fluorescence wavelengths (λ_{emi}) as well as related experimental data for these PAQ derivatives were collected in Table 2. Fabian and co-workers suggested that compounds with low extinction coefficient ($\approx 6000 \text{ l mol}^{-1} \text{ cm}^{-1}$) also had low oscillator strength (< 0.3), whereas those with high extinction coefficient ($\approx 15\,000 \text{ l mol}^{-1} \text{ cm}^{-1}$) were characterized by oscillator strength ($f \geq 0.5$) [28]. In particular, the maximum excitation wavelength (λ_{\max}^{ads}) were dominated by the HOMO-LUMO single excitation and their extinction coefficients (oscillator strength, f) distinguished the peak of excited electronic state transition with its maximum ranging from about 350 nm to 420 nm, which were generated by the highest of the oscillator strengths distinguished the peak of excited electronic state transition in the PAQ derivatives.

In this work, several different calculated methods were

used to calculate the maximum excitation wavelength (λ_{\max}^{ads}) for PAQ and its derivatives. To generate a better-calculated method in this study, we plot the experimental excitation and emission wavelength vs. calculated maximum excitation wavelength (λ_{\max}^{ads}) and fluorescence wavelength (λ_{emi}), which are shown in Figures 3, 4, 5 and 6. In the experiment, the spectra of compounds 13–18 were measured with ethyl acetate and others are with chloroform. The experimental excitation wavelength and emission wavelength of compounds 13–18 were ignored in Figures 3, 4, 5 and 6. The corresponding regression equations were given as follows:

$$\lambda_{\text{Exp}} = 0.7466\lambda_{\text{cal}} + 127.41, r^2 = 0.8603$$

(ZINDO/AM1)

$$\lambda_{\text{Exp}} = 1.1328\lambda_{\text{cal}} - 14.782, r^2 = 0.9014$$

(ZINDO/DFT)

$$\lambda_{\text{Exp}} = 2.3414\lambda_{\text{cal}} - 503.56, r^2 = 0.9288$$

(TD/DFT for excitation wavelength)

$$\lambda_{\text{Exp}} = 0.9324\lambda_{\text{cal}} + 109.77, r^2 = 0.8454$$

(ZINDO/AM1 for fluorescence wavelength)

Where λ_{Exp} and λ_{cal} are the experimental excitation wavelength and the calculated maximum excitation wavelength (or fluorescence wavelength), respectively. r^2 is the correlation coefficient. According to the above calculation results, the calculated excitation wavelength with TD/DFT method has the higher correlation coefficient r^2 (> 0.92) and generating the better linear relationship than other calculation results with experimental data. The errors were around ± 40 and ± 85 nm for excitation and flu-

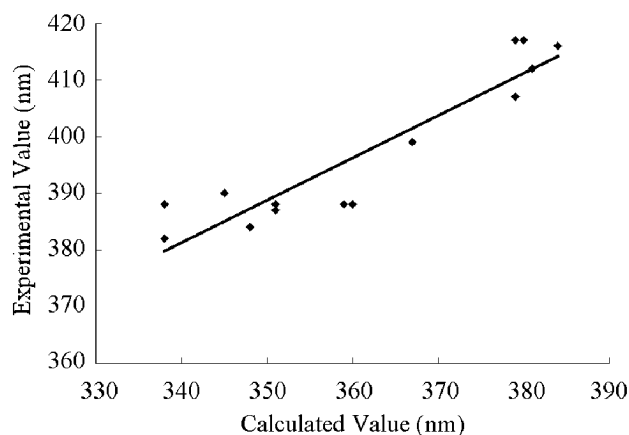


Figure 3. Plot of calculated the maximum excitation wavelength (λ_{\max}^{ads}) (ZINDO/AM1 method) vs. experimental absorption.

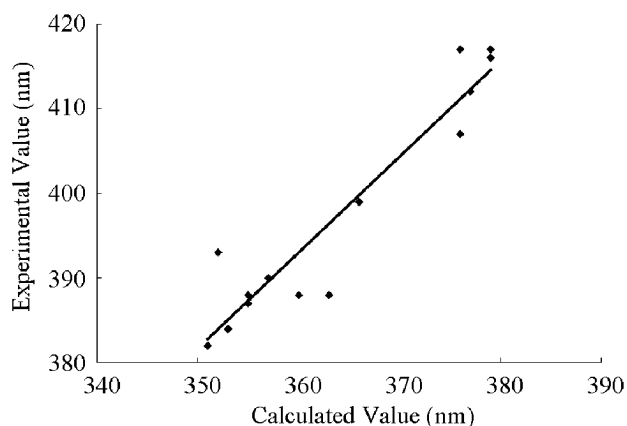


Figure 4. Plot of calculated the maximum excitation wavelength (λ_{\max}^{ads}) (ZINDO/DFT method) vs. experimental absorption.

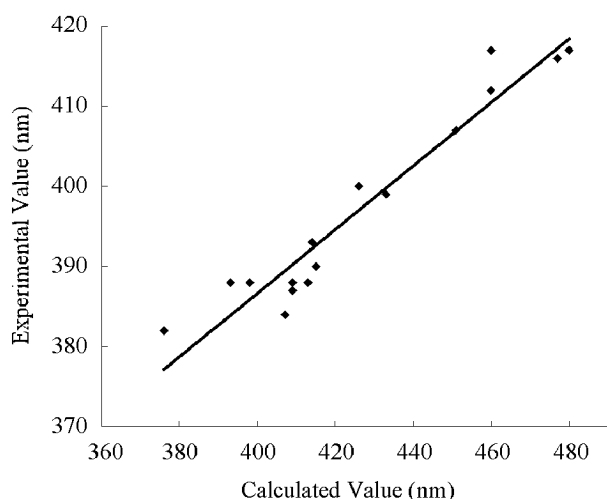


Figure 5. Plot of calculated the maximum excitation wavelength (λ_{\max}^{ads}) (TD/DFT method) vs. experimental absorption.

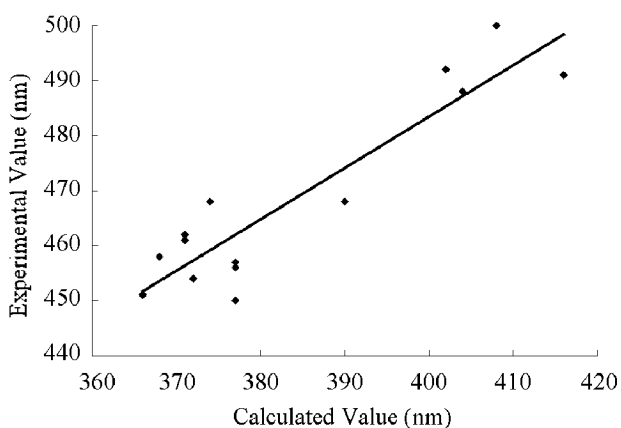


Figure 6. Plot of calculated fluorescence wavelength vs. experimental data.

orescence wavelengths, respectively.

3.2 Substitution Position Effect in PAQ Derivatives

In order to investigate the substitution effect in the excitation of PAQ derivatives, the methyl and phenyl substitutions at 1-, 3- and 4-positions of PAQ (Figure 1) were proposed. Ab initio DFT/B3LYP/6-31G* and TD/DFT/B3LYP/6-31G* calculations were used to determine the orbital energies of HOMO, LUMO and maximum excitation wavelength (λ_{\max}^{ads}) for these PAQ derivatives (Table 2).

Since methyl and phenyl substituents are electron-donating groups, they push the electron to the PAQ moiety and increase the p_{π} electron density. The orbital energy of HOMO increased more than that of LUMO for PAQ derivatives with the methyl and phenyl group at 1-, 3- and 4-substitutions. Thus, the excitation energies and the HOMO-LUMO energy gap of PAQs derivatives would decrease except the substituents at 4-position. The calculated results show that the PAQ with the methyl and phenyl groups generate the red-shifted excitation wavelength comparing to the PAQ without any substituent. The 4-substituted PAQ (except compounds 9 and 11) decrease the excitation energy and generate the blue-shifted excitation wavelength comparing to PAQ. We compared the calculated results for two sets of compounds 3, 5 and 9, 11, all of them are 1,3-substituted PAQ with methyl and phenyl substituents and without 4-substitution for compounds 3, 5. According to Table 2, compounds 3, 5 (1,3-substituted PAQ) have blue-shifted calculated maximum excitation wavelength to those of compounds 9, 11 (1-,3-,4-substituted PAQ). Since compounds 9 and 11 have 4-substitution in PAQ and it may cause the steric effect in these PAQ derivatives. Comparing the optimized structures of compounds 9–12, which are the 1-,3-, 4-substituted PAQ and the methyl group at 3-substitution, the dihedral angle (α) is between PAQ moiety and the phenyl substituents for 4-substitution increasing due to the steric effect. The calculated dihedral angle (α) at compounds 11 and 12 are 75.3° and 64.2°, respectively. The calculated results (Table 2) indicated that the substitution position effect increases as the following: 1- > 3- in the PAQ derivatives. For the maximum excitation wavelength (λ_{\max}^{ads}) of PAQ derivatives, 3-phenyl PAQ has higher oscillator strength than that of the methyl substituted or no-substituent PAQ. This conclusion generates a good

Table 2. Calculated maximum excitation wavelength ($\lambda_{\max}^{\text{abs}}$, nm) (by ZINDO/AM1, ZINDO/DFT/6-31G* and TD-DFT/B3LYP/6-31G*), fluorescence (λ_{emi} , nm) (by ZINDO/AM1) as well as the experimental excitation wavelength ($\lambda_{\max}^{\text{abs}}$, nm) and fluorescence (λ_{emi} , nm) of PAQ and its derivatives

| Cpd ^a | Calculated value | | | | Experimental value | |
|------------------|-------------------------------|------------------------|-------------------------------|-------------------------------|-------------------------------|------------------------|
| | ZINDO/AM1 ^b | | ZINDO/DFT ^c | TD-DFT ^c | $\lambda_{\max}^{\text{abs}}$ | λ_{emi} |
| | $\lambda_{\max}^{\text{abs}}$ | λ_{emi} | $\lambda_{\max}^{\text{abs}}$ | $\lambda_{\max}^{\text{abs}}$ | | |
| PAQ | 341 | 360 | 346 | 346 | — | — |
| 1 | 343 | 362 | 350 | 358 | — | — |
| 2 | 336 | 359 | 346 | 352 | — | — |
| 3 | 346 | 363 | 352 | 366 | — | — |
| 4 | 359 | 384 | 360 | 398 | 388 ^d | 438 ^d |
| 5 | 351 | 372 | 355 | 409 | 387 ^d | 454 ^d |
| 6 | 367 | 390 | 366 | 433 | 399 ^d | 468 ^d |
| 7 | 350 | 371 | 355 | 409 | — | — |
| 8 | 351 | 371 | 355 | 409 | 388 ^c | 461 ^c |
| 9 | 351 | 371 | 355 | 409 | 388 ^c | 462 ^c |
| 10 | 352 | 372 | 355 | 409 | — | — |
| 11 | 360 | 377 | 363 | 413 | 388 ^c | 456 ^c |
| 12 | 348 | 366 | 353 | 407 | 384 ^c | 451 ^c |
| 13 | 345 | 377 | 357 | 415 | 390 ^c | 457 ^c |
| 14 | 338 | 372 | 351 | 376 | 382 ^d | 427 ^d |
| 15 | 338 | 377 | 355 | 393 | 388 ^d | 450 ^d |
| 16 | 342 | 368 | 352 | 414 | 393 ^d | 458 ^d |
| 17 | 339 | 374 | 353 | 426 | 400 ^d | 468 ^d |
| 18 | 365 | 387 | 366 | 397 | — | — |
| 19 | 368 | 389 | 371 | 403 | 412 ^f | 442 ^f |
| 20 | 364 | 391 | 365 | 407 | 398 ^f | 446 ^f |
| 21 | 363 | 395 | 363 | 421 | 398 ^f | 468 ^f |
| 22 | 377 | 408 | 392 | 447 | 451 ^f | 521 ^f |
| 23 | 365 | 387 | 366 | 396 | 388 ^f | 434 ^f |
| 24 | 364 | 395 | 364 | 417 | 399 ^f | 446 ^f |
| 25 | 375 | 401 | 371 | 448 | — | — |
| 26 | 381 | 408 | 377 | 460 | 412 ^d | 500 ^d |
| 27 | 379 | 402 | 379 | 460 | 417 ^d | 492 ^d |
| 28 | 380 | 410 | 376 | 480 | 417 ^d | 532 ^d |
| 29 | 379 | 404 | 376 | 451 | 407 ^d | 488 ^d |
| 30 | 384 | 416 | 379 | 477 | 416 ^d | 491 ^d |

^a The molecular structures of PAQ and its derivatives are shown in Figure 2. ^b The geometries of PAQ and its derivatives were optimized by AM1. ^c The geometries of PAQ and its derivatives were optimized by DFT(B3LYP/6-31G*). ^d ref [23], ^e ref [21], ^f ref [22].

agreement with the experiment.

3.3 Substituent Effect in PAQ Derivatives

Besides substitution position effect, we used the DFT B3LYP and TD/DFT/B3LYP calculation methods to determine the HOMO, LUMO orbital energies and the maximum excitation wavelength ($\lambda_{\max}^{\text{abs}}$) of PAQ derivatives with different substituents. Table 4 showed the calculated molecular orbital energies of HOMO and LUMO for these PAQ derivatives. Compounds 5 and 13–16 are

different alkyl substituents at 3-substituted PAQ (Figure 1). There are similar calculated HOMO and LUMO orbital energies and the energy gap (ΔE) for these PAQ derivatives. The differences of the calculated energy gap (ΔE) (0.131 eV, 0.131 eV, 0.132 eV, 0.132 eV and 0.131 eV) of methyl, ethyl, propyl, n-butyl and tert-butyl substituents at the 3-substituted PAQ derivatives are varying small.

In order to investigate the influences of different substituents at the 6-substituted PAQ derivatives, -F,

-CN electron withdrawing and -Me, -OMe, -NEt₂, -*t*-Bu electron-donating substituents were used for these PAQ derivatives (Compounds 18–23 and 25–29, Figure 1). The calculated HOMO, LUMO and the maximum excitation wavelength ($\lambda_{\text{max}}^{\text{ads}}$) for these PAQ derivatives were calculated by ab initio DFT and TD/DFT method, the calculation results were shown in Tables 2 and 5. Since the electron-withdrawing group reduced the p electron density in the parent PAQ ring. Thus, both the orbital energies of HOMO and LUMO were decrease by the electron-withdrawing substituent in the PAQ derivatives. According to the electronic structure analysis, the orbital energy of LUMO decreased much more than that of HOMO in the PAQ derivatives with the electron-withdrawing substituent at the 6-position and the energy gap ($\Delta E = \text{LUMO} - \text{HOMO}$) of them would decrease. Thus, the electron-withdrawing substituent resulted in a red-shifted excitation wavelength to the non-substituent at the 6-position of PAQ (compound 4 vs. compounds 20–21 and compound 25 vs. compounds 26, 28). The substituent effect in the PAQ derivatives with the electron-withdrawing substituent at the 6-position has the following order: -CN > -F. This order agrees very well with the deactivation order of an aromatic ring in organic chemistry.

On the contrast, the PAQ derivatives with electron-donating substituent increased the p_{π} electron den-

Table 3. DFT/B3LYP/6-31G* calculated HOMO(eV), LUMO(eV) and $\Delta E (= \text{LUMO} - \text{HOMO})$ (eV) for the 1-, 3-, 4-substituted PAQ

| Cpd ^a | DFT | | |
|------------------|--------|--------|------------|
| | HOMO | LUMO | ΔE |
| PAQ | -0.215 | -0.068 | 0.147 |
| 1 | -0.209 | -0.066 | 0.144 |
| 2 | -0.210 | -0.065 | 0.146 |
| 3 | -0.205 | -0.063 | 0.142 |
| 4 | -0.201 | -0.069 | 0.131 |
| 5 | -0.201 | -0.070 | 0.131 |
| 6 | -0.199 | -0.075 | 0.124 |
| 7 | -0.198 | -0.067 | 0.131 |
| 8 | -0.198 | -0.070 | 0.129 |
| 9 | -0.200 | -0.062 | 0.138 |
| 10 | -0.199 | -0.067 | 0.133 |
| 11 | -0.198 | -0.068 | 0.130 |
| 12 | -0.215 | -0.068 | 0.147 |

^a The molecular structures of the PAQ and relative derivatives are shown in Figures 1 and 2.

sity in the PAQ moiety, and the orbital energies of HOMO and LUMO increases. According to the electronic structure analysis, the orbital energy of LUMO increased much more than that of HOMO in compounds 18 and 23 and their energy gap (ΔE) increase. The electron-donating substituent resulted in a blue-shift excitation wavelength to the non-substituent at the 4-position of PAQ (compounds 4 vs. compounds 18 and 23), but the results of compounds 19 (6-OCH₃-PAQ) and 22 (6-NEt₂-PAQ) were just the opposite. The orbital energy difference of LUMO between compounds 4 and 19 or 22 was larger than that of compounds 4 and 18 or 23. According to the electronic structure analysis, the mixing of the lone pair electrons on the nitrogen or oxygen into the HOMO orbital would raise the HOMO level

Table 4. DFT/B3LYP/6-31G* calculated HOMO(eV), LUMO(eV) and $\Delta E (= \text{LUMO} - \text{HOMO})$, eV) for the 3- alkyl PAQ

| Cpd ^a | DFT | | |
|------------------|--------|--------|------------|
| | HOMO | LUMO | ΔE |
| 5 | -0.202 | -0.070 | 0.131 |
| 13 | -0.201 | -0.069 | 0.131 |
| 14 | -0.200 | -0.069 | 0.132 |
| 15 | -0.200 | -0.069 | 0.132 |
| 16 | -0.201 | -0.069 | 0.131 |

^a The molecular structures of the derivatives are shown in Figure 2.

Table 5. DFT/B3LYP/6-31G* calculated HOMO(eV), LUMO(eV) and $\Delta E (= \text{LUMO} - \text{HOMO})$, eV) for the 6-, 7- substituted PAQ

| Cpd ^a | DFT | | |
|------------------|--------|--------|------------|
| | HOMO | LUMO | ΔE |
| 4 | -0.201 | -0.069 | 0.131 |
| 18 | -0.198 | -0.067 | 0.131 |
| 19 | -0.195 | -0.065 | 0.129 |
| 20 | -0.203 | -0.075 | 0.129 |
| 21 | -0.215 | -0.089 | 0.126 |
| 22 | -0.175 | -0.058 | 0.117 |
| 23 | -0.198 | -0.066 | 0.132 |
| 25 | -0.193 | -0.073 | 0.121 |
| 26 | -0.196 | -0.078 | 0.118 |
| 27 | -0.187 | -0.071 | 0.117 |
| 28 | -0.205 | -0.091 | 0.114 |
| 29 | -0.191 | -0.071 | 0.120 |

^a The structures of the PAQ derivatives are shown in Figure 2.

more and decrease the energies gap (ΔE). The electron-donating substituent resulted a red-shift excitation wavelength as compared to the PAQ derivatives without any R₄ substitution (compound 4 vs. 19 and compound 25 vs. 27). The substituent effect in the PAQ derivatives with the electron-withdrawing/donating substituent at the 6- position had the follow order: -NEt₂ > -CN > -F > -OMe > -t-Bu \approx -Me.

4. Conclusions

The experiments had demonstrated that the PAQ derivatives could be used as dopants in the multi-layer OLED fabrication. In this study, the maximum excitation wavelength ($\lambda_{\max}^{\text{ads}}$) was calculated by ab initio TD-DFT and the semiempirical ZINDO methods. These calculated data generated an excellent agreement with the linear relationship between experimental and calculated absorption $\lambda_{\max}^{\text{ads}}$ than by the calculated ZINDO/AM1 method. We used the ab initio DFT and TD-DFT calculated methods to investigate the substitution position effect and substituents effect in the PAQ derivatives. The maximum excitation wavelength ($\lambda_{\max}^{\text{ads}}$) of PAQ derivatives with the methyl and phenyl substituents have red-shifted excitation wavelength to the PAQ derivatives without 1- and 3- substitution; the substitution position effect for these PAQ derivatives increase as the following order 1- > 3-. Besides, the 3-phenyl-PAQ has higher oscillator strength than that of the 3-methyl PAQ both for the calculations and experimental work. 4-methyl-PAQ and 4-phenyl-PAQ have the blue-shifted excitation wavelength to the PAQ derivatives with non-substituent at the 4-position of PAQ except 3-methyl-4-phenyl-PAQ. 3-alkyl-PAQ with different alkyl group generates a smaller substituent effect than that of PAQ compound. For 6-substituted PAQ, the electron-withdrawing substituent determined a red-shifted excitation wavelength to the non-substituent at the 6-position of PAQ. Except compounds 19 (6-OCH₃-PAQ) and 22 (6-NEt₂-PAQ), electron-donating substituent resulted in a blue-shifted excitation wavelength to PAQ compound. Actually, most of the above calculation results have been confirmed by the related experimental data. This calculation could be used as a model system for understanding the relation between the spectral property and the optimized structure of PAQ derivatives and could be employed to explore the poten-

tial EL device and their applications also.

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