# Spectroscopic properties of carbazolyl and diphenylamino naphthalimide derivatives: the role of solvent and rotational relaxation

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The absorption and emission spectra of a series of 4-carbazolyl/4-diphenylamino-N-(H-, methyl, cyclohexyl, phenyl)-1, 8-naphthalimide derivatives in gas-phase have been calculated using TD-B3LYP/6-31G* approaches. With different substituents on the *N*-imide group and naphthalimic group, their optical properties in solvent have also been studied by C-PCM model. Result show that there are three peaks in the absorption spectra. For absorption spectra, the third peak, similar to the luminescent peak emitted by diphenylamine or carbazoly, the second peak, similar to the luminescence emitted by the 1, 8-naphthalimide, and a considerable long-wavelength luminescent are observed. The extended conjugation comprising the carbazolyl and naphthalimide moieties, attributed to the coplanar geometry, endows the first peak excited state with charge transfer property.

## 1. Introduction

1, 8-naphthalimide derivatives have found numerous applications in various fields due to their luminescent properties. High electron affinities, [1] wide gap, [2,3] and low reduction potentials, [4] make them good candidates in organic light emitting diodes (OLEDs) as n-type materials [5]. They are also applied in sensitizers for Grätzel solar cell, [6,7] to the logic gate, [8] sensor [9] and charge separation mimic, [10] where they act as electron acceptor, [11,12] or electron donor [10] or energy donor [13]. Besides, they are utilized as the connected units of dendrimer to probe the dynamic protein interactions [14].

Numerous research efforts have been directed through the molecular engineering and device configuration [15-19]. However, there are still a lot challenges including maximization of the external quantum efficiency, to design and synthesis new materials for tunable colors and models of addressing devices for a full color display with optimized resolution. This has prompted synthetic chemists to constitute some chromophores in an effort both to tune their electronic properties and to improve their quantum yields [16,20,21]. In previous publications we explored the absorption and emission spectra of 4-carbazolyl-N-methyl/phenyl-1,8-naphthalimide derivatives [16]. The naphthalimide derivatives with carbazole (NC) emit fluorescence at 440-580 nm in various solvents with different polarities. NC is composed of the carbazolyl and naphthyl moieties connected by the C-N bond, which can freely rotate as 4-(dimethylamino), 9-9-bianthryl and N-phenylphenanthridionoes. The rotation can thus give rise to the extended conjugation and charge transfer differs in the different rotation angles, which is easy to be affected by the solvent polarities.

In previous publication [2,22,23], N-phenylnaphthalimides showed red-shifted long-wavelength (LW) fluorescence apart from short-wavelength (SW) emission, which yield by the solvent and geometrical relaxation. SW is in the same spectra region as that of N-alkylnaphthalimide and a strong red-shifted and LW fluorescence is from ICT state. It is clear that the carbazole can rotate freely, which suggest that the rotation of carbazole group can either on or off, providing not only a sensitive measure of the local environment but also a means to determine whether the fluorescent probe is truly "off" or is simply absent due to some type of photo- or chemical degradation process. Some semi-empirical calculations and DFT calculations have been reported for some naphthalimides [24-27]. In our investigation of the naphthalimide derivatives, attention is directed to the nature the absorption, fluorescence states as well as to the kinetics and mechanism of the photophysical processed taking place in these naphthalimide derivatives. Structures, names and acronyms (in brackets) of the 1, 8-naphthalimide derivatives are given below.

## 2. Computation methods

All calculations have been carried out with Gaussian 03 suite of programs [28], with systematically tightened SCF convergence and geometry optimizations (rms force $<1.0 \times 10^{-5}$ a.u.) criteria in order to ensure numerically accurate results. B3LYP [29,30] has been selected for all DFT and TDDFT computations and a 6-31G(d) basis set have been used. For these derivatives with no symmetry constraint, the ground-state ($S_0$) and the first singlet excited-state ($S_1$) have been optimized by CIS methods.

These minimizations have been performed by the HF ($S_0$), B3LYP ($S_0$), CIS ($S_1$) approaches. Vertical ionization potentials (VIP) were calculated by subtracting the total energy of the neutral molecules from those of charged molecules at neutral equilibrium geometries. Natural population analysis [31,32] and natural bond orbitals [33] were carried out to compute atomic charges and energy analysis. Their electronic delocalization energies were also quantitatively assessed by deleting substituents or naphthalimic rings, or specific NBO donor-acceptor interactions as implemented in the NBO3.1 [34] contained in Gaussian package. They were obtained by subtracting the energy of the natural Lewis structure from original ground state energy.

## 3. Results and discussion

### 3.1 Geometries of naphthalimide derivatives in the $S_0$ and $S_1$ states

Naphthalimide derivatives can be treated as a combination of three subsystems; viz. substituent (R) in the top position, naphthalimide (NI) moiety in the middle and substituents such as carbazolyl or diphenylamino group (SU) at the bottom position, as shown in Fig. 1. Selected optimized bond lengths and bond angles of $S_0$ and $S_1$ calculated at B3LYP/6-31G*, HF/6-31G* and CIS/6-31G* are summarized in the Table 1, along with bond distances which has been determined from the X-ray structure analysis [16]. Theoretical bond lengths are a little longer than the experimental values, which is at least partly due to solid state effect [35]. The geometry parameters investigated by B3LYP/6-31G* are very similar to those results by HF/6-31G*, with a little longer C=O bond lengths. Comparison between the $S_0$ and $S_1$

state geometries for these compounds indicates the contraction of B1 and B2 bond lengths, suggesting strengthened interaction between SU and NI moieties in the $S_1$ state. The contraction of dihedrals between SU and NI also occurred from the $S_0$ to the $S_1$ state for those geometries. Thus, the excitation from $S_0$ to $S_1$ might cause significant structure change. Fig. 1 illustrates the scheme and the bond labels used in Table 1. Inspection of Table 1 also shows that bond lengths of B1 and B2 increase and bond indexes decreases when two phenyls are bridged by C-C bond. The increase of delocalization electronic energies suggests that the interactions between naphthalene and substituents are intensified. The relative bond length deviation between HF and CIS is under the range of 0.002 Å.



R=H-, methyl, cyohexane-chair, phenyl

They are in the order of I, II, III, IV, V, VI, VII, VIII, which are consist of R, NI and SU(diphenyl or carbazolyl) fragments.  B1 and B2 stands for different bond length.
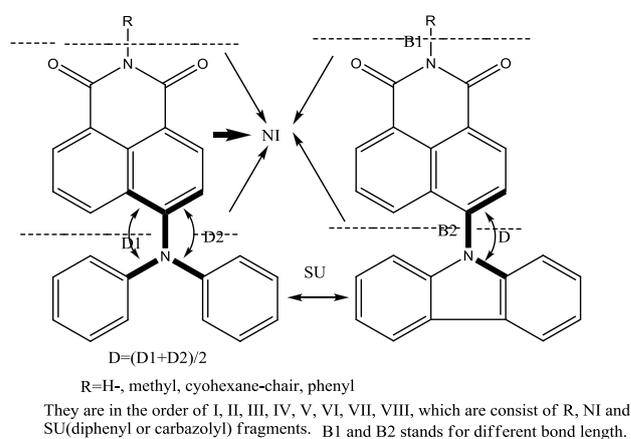
*Fig. 1. 4-carbazolyl/4-diphenylamino-N-(H-, methyl, cyclohexyl, phenyl)-1,8-naphthalimide derivatives studied in this project.*

*Table 1. Calculated geometrical parameters, charges and delocalization electronic energies by B3LYP, HF and CIS approaches*

| B3LYP | III | IV | V | VI |
|---|---|---|---|---|
| bond indexes (1) | 0.937 | 0.936 | 0.934 | 0.930 |
| bond indexes (2) | 1.022 | 0.977 | 1.022 | 0.975 |
| $D^a$ | 56.4 | -69.7 | 50.3 | 62.9 |
| Delocalization (R/NI)/(kcal.mol$^{-1}$) | 1961.3 | 2049.4 | 2323.4 | 2399.6 |
| Delocalization(NI/SU) /(kcal.mol$^{-1}$) | 33.27 | 47.90 | 42.59 | 47.58 |
| $q_R$ | 0.261 | 0.264 | 0.240 | 0.254 |
| $q_{NI}$ | -0.140 | -0.191 | -0.119 | -0.0607 |
| $q_{SU}$ | -0.120 | -0.0731 | -0.121 | -0.1935 |
| B1/Å | 1.466 | 1.467 | 1.447 | 1.448 |
| B2/ Å | 1.419 | 1.420 | 1.419 | 1.420 |
| Dipole/(Debye) | 5.15 | 2.83 | 4.95 | 2.43 |

| Compound | $S_0$/HF | | | $S_1$/CIS | | |
|---|---|---|---|---|---|---|
| | B1 | B2 | $D^a$ | B1 | B2 | $D^a$ |
| III | 1.463 | 1.417 | 54.54 | 1.462 | 1.382 | 47.51 |
| IV | 1.464 | 1.417 | 89.89 | 1.462 | 1.385 | 120.0 |
| V | 1.441 | 1.417 | 56.64 | 1.439 | 1.382 | 47.00 |
| VI | 1.442 | 1.417 | 89.70 | 1.440 | 1.385 | 51.42 |

## 3.2 Vertical excitation energies in vacuo and different solvents

We calculate the vertical absorption and emission transition and the frontier orbitals of the naphthalimide derivatives using the optimized geometries of the $S_0$ and $S_1$ state with B3LYP/6-31G*, HF/6-31G* and CIS/6-31G* methods. The first lowest singlet excitation between $S_0$ and $S_1$ in gas phase, as shown in Table 2, corresponds predominantly the electronic transition from HOMO to LUMO.

Their frontier orbitals in Fig. 2 indicate the delocalized electronic density. HOMO is mainly localized on the rigidity naphthalimic ring while the LUMO is predominantly localized on the NI moiety, but it leaves a few contributions on R substituents which are almost identical to the anti-bonding patterns between substituents and NI moiety. Substituents in the imide position have a few influences on the wavenumbers of $S_0$ and $S_1$ but intensify the oscillator strength for compounds having diphenylamino groups. Oscillator strengths increase in the order of the electron-donation ability of the substituent from H-, methyl, chair-cyclohexyl to phenyl. The location of the long wavelength of the first excited state is not sensitive to substituents on the imide position.
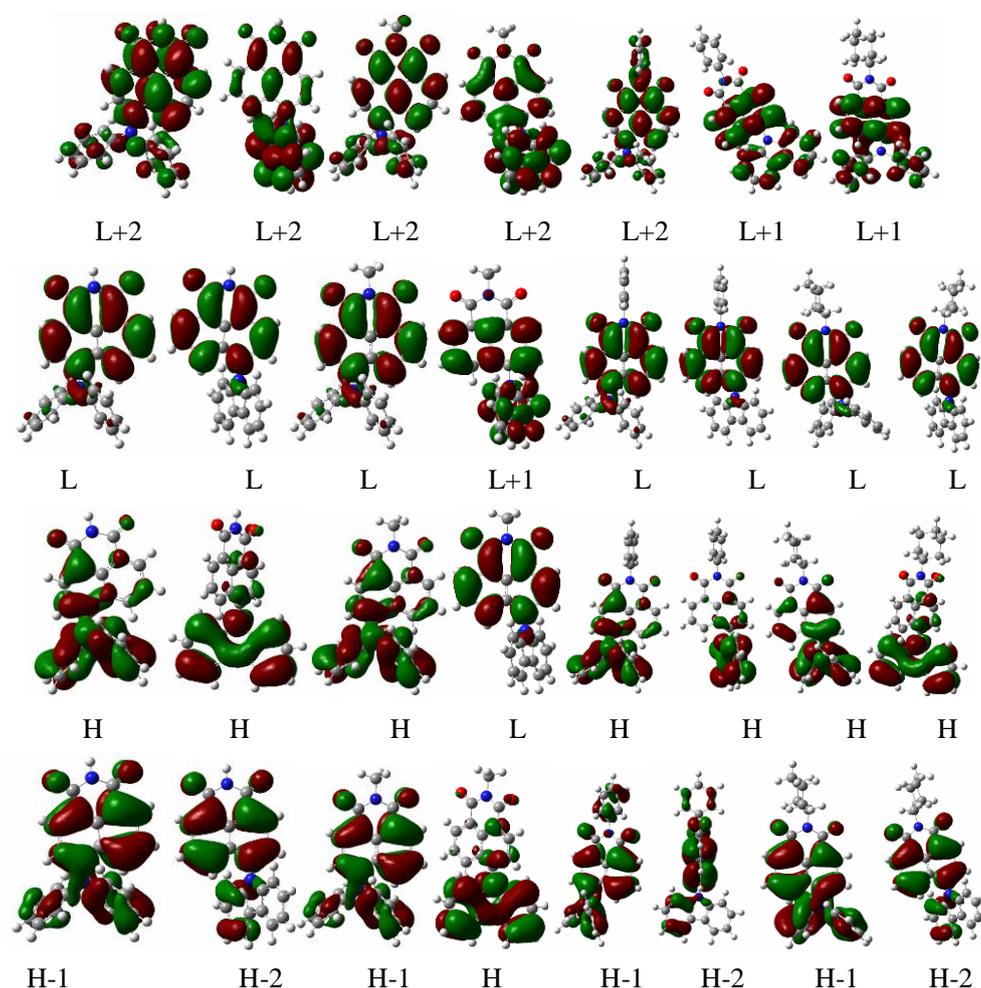


Fig. 2. Selected HOMOs and LUMOs of the $S_0$ Geometry computed with the B3LYP/6-31G* scheme

As we can see from Table 2, three peaks are shown in their absorption and emission spectra. The first lowest singlet excitation of carbazole lies at about 299 nm with oscillator strength 0.0288 in gas phase while that of 1, 8-naphthalimide lies at about 339 nm with oscillator strength 0.0001 within framework of TD-B3LYP/6-31G* model. Compared to the vertical absorption properties of 1, 8-naphthalimide and carbazole, the third peak at about 303 nm, might correspond to the original fluorescent spectra of carbazole. The second peak, about 364 nm, might

correspond to the fluorescence peak of 1, 8-naphthalimide. The oscillator strength increased once the separated units were connected together. The oscillator strength is much weaker in absorption spectra, which might be neglected by the experimental measurement. The first peak corresponds to the intramolecular charge transfer (ICT).

From $S_0$ to $S_1$, red-shifted wavelength and the strengthened intensity occur as a result of configuration change. Bigger change takes place on diphenylamino compounds than those carbazolyl compounds, which suggests the relaxation energies resulted from steric diphenylamine are greater than those carbazolyls. The intensities of the second and the third peak are reduced from $S_0$ to $S_1$.

In order to properly compare the CPCM-TDDFT excitation energies reported in Table 2, it is better to compare gas-to-solvent shifts instead of absolute energies. Solvent or the relaxations of inner configuration exert a few influences on the location of the second and third peak while they impose much more influence on the location of the first peak. From nonpolar solvents to polar solvents, the intensity of the third peak decreases with increased polarity of the medium while the intensity of the second and the first peak increase. Absorption maxima of compounds containing carbazolyls shift about 10 nm in $C_2H_2Cl_2$ and 11 nm in HCN. Absorption maxima of compounds containing diphenylamino groups shift about 20 nm in chair-cyclohexyl and 37 nm in $C_2H_2Cl_2$. Solvent induced shifts of emission maxima are similar to those absorption spectra determined by carbazolyls or diphenylamino groups.

*Table 2. Calculated absorption and emission vertical transition parameter in different solvent. (The unit of excitation energy (E.E) are in eV(nm))*

| | Absorption | | | Emission In $C_2H_2Cl_2$ | | |
|---|---|---|---|---|---|---|
| | E.E | f | Configuration | E.E | f | Configuration |
| I-$C_6H_{12}$ | 2.51(495) | 0.234 | H-0->L+0(+92%) | 2.44(509) | 0.228 | H-0->L+0(+92%) |
| | 3.73(333) | 0.291 | H-1->L+0(+81%) | 3.69(336) | 0.129 | H-1->L+0(+82%) |
| | 4.13(300) | 0.183 | H-3->L (+23%) | 4.00(309) | 0.128 | H-0->L+2(+36%) |
| | | | H-0->L+2(+68%) | | | H-3->L   (+40%) |
| II-$C_6H_{12}$ | 2.50(497) | 0.0693 | H-0->L+0(+97%) | 2.41(514) | 0.198 | H-0->L+0(+91%) |
| | 3.65(340) | 0.291 | H-2->L+0(+84%) | 3.41(364) | 0.217 | H-2->L+0(+83%) |
| | 4.09(303) | 0.085 | H-0->L+1(+50%) | 4.09(303) | 0.0989 | H-0->L+2(+88%) |
| | | | H-0->L+1(+34%) | | | |
| III- $C_6H_{12}$ | 2.51(493) | 0.241 | H-0->L+0(+92%) | 2.35(528) | 0.334 | H-0->L+0(+86%) |
| | 3.72(333) | 0.140 | H-1->L+0(+82%) | 3.55(349) | 0.0919 | H-1->L+0(+85%) |
| | 4.12(301) | 0.193 | H-0->L+2(+73%) | 4.07(305) | 0.126 | H-0->L+2(+54%) |
| | | | | | | H-3->L (+33%) |
| IV-HCN | 2.48(501) | 0.057 | H-0->L+0(+97%) | 2.42(512) | 0.204 | H-0->L+0(+91%) |
| | 3.62(343) | 0.307 | H-2->L+0(+84%) | 3.40(365) | 0.221 | H-2->L+0(+83%) |
| | 4.09(303) | 0.077 | H-0->L+1(+83%) | 4.09(303) | 0.0983 | H-0->L+1(+88%) |
| V- $C_2H_2Cl_2$ | 2.43(509) | 0.256 | H-0->L+0(+92%) | 2.47 (502) | 0.240 | H-0->L+0(+92%) |
| | 3.72(337) | 0.152 | H-1->L+0(+81%) | 3.66(339) | 0.171 | H-1->L+0(+79%) |
| | 3.93(315) | 0.144 | H-0->L+1(+64%) | 4.03(308) | 0.048 | H-3->L+0(+50%) |
| | | | | | | H-0->L+0(+33%) |
| VI- $C_2H_2Cl_2$ | 2.48(500) | 0.0613 | H-0->L+0(+97%) | 2.43(511) | 0.219 | H-0->L+0(+91%) |
| | 3.62(343) | 0.315 | H-2->L+0(+84%) | 3.39(366) | 0.240 | H-2->L+0(+83%) |
| | 4.09(303) | 0.0807 | H-0->L+1(+84%) | 4.08(304) | 0.095 | H-0->L+1(+87%) |
| VII HCN | 2.51 (494) | 0.254 | H-0->L+0(+92%) | 2.35(528) | 0.361 | H-0->L+0(+87%) |
| | 3.71(334) | 0.165 | H-1->L+0(+83%) | 3.55(349) | 0.105 | H-1->L+0(+85%) |
| | 4.10(302) | 0.194 | H->L+1(+73%) | 4.00(310) | 0.146 | H-0->L+1(+48%) |
| | | | | | | H-0->L+2 (+27%) |
| VIII- $C_2H_2Cl_2$ | 492(2.52) | 0.076 | H-0->L+0(+97%) | 2.42(512) | 0.222 | H-0->L+0(+91%) |
| | 3.62(342) | 0.343 | H-2->L+0(+84%) | 3.39(365) | 0.250 | H-2->L+0(+83%) |
| | 4.08(304) | 0.086 | H-0->L+1(+84%) | 4.09(303) | 0.113 | H-0->L+1(+88%) |

| Gas | absorption | TD-B3LYP/6-31G* | | Gas | emission | |
| | E.E | f | Configuration | E.E | f | Configuration |
|---|---|---|---|---|---|---|
| I | 2.62(474) | 0.179 | H-0->L+0(+90%) | 2.52(493) | 0.249 | H-0->L+0(+84%) |
| | 3.79(327) | 0.091 | H-1->L+0(+74%) | 3.62(340) | 0.0662 | H-1->L+0(+83%) |
| | 4.21 (295) | 0.151 | H-0->L+2(+67%) | 4.18 (296) | 0.143 | H-1->L+3(+80%) |
| II | 2.50(496) | 0.0501 | H-0->L+0(+97%) | 2.47 (501) | 0.142 | H-0->L+0(+89%) |
| | 3.71(334) | 0.202 | H-2->L+0 (79%) | 3.48(356) | 0.127 | H-2->L+0(+59%) |
| | 4.11 (302) | 0.065 | H-0->L+2 (80%) | 4.11(302) | 0.067 | H-0->L+1(+83%) |
| III | 2.63(472) | 0.188 | H-0->L+0(+90%) | 2.53 (490) | 0.264 | H-0->L+0(+83%) |
| | 3.79(327) | 0.104 | H-1->L+0(+78%) | 3.64(341) | 0.0677 | H-1->L+0(+83%) |
| | 4.21 (295) | 0.168 | H-0->L+2(+79%) | 4.16(298) | 0.119 | H-0->L+2(+69%) |
| IV | 2.53(490) | 0.053 | H-0->L+0(+97%) | 2.49 (498) | 0.150 | H-0->L+0(+89%) |
| | 3.71(334) | 0.222 | H-2->L+0(+80%) | 3.46(358) | 0.136 | H-2->L+0(+64%) |
| | 4.11(302) | 0.055 | H-0->L+2(+45%) | 4.09(303) | 0.055 | H-0->L+1(+83%) |
| | | | H-0->L+1(+33%) | | | |
| V | 2.63(472) | 0.209 | H-0->L+0(+90%) | 2.53 (490) | 0.295 | H-0->L+0(+84%) |
| | 3.77(329) | 0.101 | H-1->L+0(+74%) | 3.64(341) | 0.0807 | H-1->L+0(+83%) |
| | 4.13(300) | 0.154 | H-0->L+2(+72%) | 4.17(298) | 0.146 | H-0->L+3(+73%) |
| VI | 2.53(490) | 0.0546 | H-0->L+0(+97%) | 2.50(496) | 0.168 | H-0->L+0(+89%) |
| | 3.68(337) | 0.168 | H-2->L+0(+65%) | 3.46(358) | 0.200 | H-2->L+0(+80%) |
| | 4.11(302) | 0.0691 | H-0->L+2(+49%) | 4.10(303) | 0.0689 | H-0->L+1(+82%) |
| | | | H-0->L+1(+26%) | | | |
| VII | 2.62(473) | 0.205 | H-0->L+0(+90%) | 2.53(490) | 0.295 | H-0->L+0(+84%) |
| | 3.77(329) | 0.126 | H-1->L+0(+79%) | 3.64(341) | 0.0807 | H-1->L+0(+83%) |
| | 4.15(299) | 0.154 | H-0->L+2(+83%) | 4.16(303) | 0.146 | H-0->L+2(+37%) |
| VIII | 2.54(489) | 0.205 | H-0->L+0(+97%) | 2.50(496) | 0.205 | H-0->L+0(+89%) |
| | 3.70(335) | 0.260 | H-2->L+0(+79%) | 3.45(359) | 0.126 | H-2->L+0(+74%) |
| | 301(4.10) | 0.054 | H-0->L+1(+68%) | 303(4.10) | 0.061 | H-0->L+1(+58%) |
| | 289(4.29) | 0.045 | H-0->L+3(+46%) | 284(4.36) | 0.0665 | H-0->L+3(+86%) |

### 3.3 Rotation of benzene, diphenylamine, carbazole for IV and VI

In order to explore their optical features, the energy levels, excitation energies, delocalization energies, dipole moments and bond indices of IV and VI are investigated. Inspection of Fig. 3 shows that energy level reaches the lowest point at about $60°$ and $120°$ and a local minimum at about $90°$. Dipole moment reduces to a global minimum at $90°$. The second peak, short wavelength-emitting state, is characterized by rather small dipole moment while the first peak, long wavelength-emitting state is characterized by very large dipole moment. Bond index and the delocalization electronic energy come to the lowest point at $90°$, suggesting their overlap diminishes for the configuration and unpaired electron density when the carbazolyl and naphthalimic ring decoupled at vertical intersection.
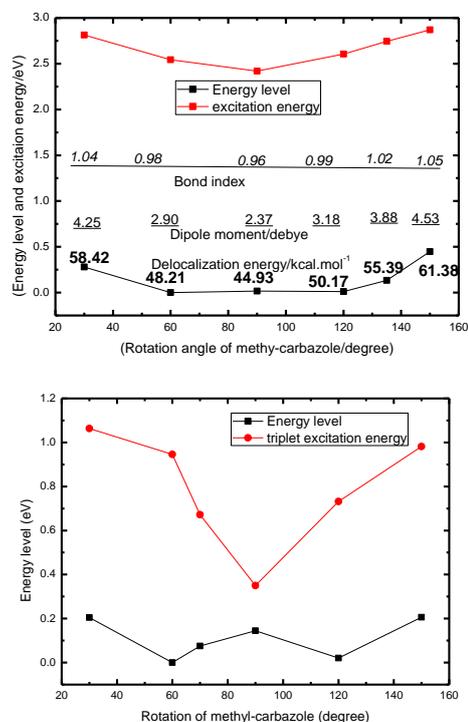




*Fig. 3. Rotation energy (singlet and triplet) curves as a function of twisted carbazole configuration for the 4-carbazolyl-N-methyl-1,8-naphthalimide*

For IV, the 90° methyl-carbazolyl derivative only shows dual obvious peak, with dominant second peak and third peak. The first peak disappears with weak oscillator strength. And the second absorption peak comes into prominence at 90° at the cost of the first absorption peak of the ICT state. On the other hand, the 0° coplanar geometry shows the first and the third peak. The ICT is the predominant peak. The second peak disappears. The change in the nature of the ICT state is reflected by the values of the oscillatory strength; from the large value characterizing the planar structure, it decreases almost to zero for completely decoupled subunits, thus indicating a transformation from the allowed π-π* to the forbidden n-π* transition. From 90° to 0°, dipole moment increase gradually. Rotation propels internal transition between the first peak and the second peak. Above phenomena make us tentatively interpret them in terms of rotation of carbazolyl group. For the carbazolyl rotation of IV in triplet state, molecule come to a local minimum and its excitation is the lowest of all at 90°. There exist two lower points distributed along the left and right side of 90°. Due to lower triplet excitation energy, the increased gap between singlet and triplet might be the cause of possible cause of high quantum yield of 4-carbazolyl -1, 8-naphthalimide derivatives.

As we can see from the Fig. 4, two global minima are also located on the right and left side of the 90° configuration of VI, which is a local minimum as that illustrates in the rotation of methyl-carbazole. The curve trend of the excitation energy is also similar to that of the methyl-carbazole. Owning to its symmetry, 90° configuration came to the lowest dipole, the interaction distance shortened, delocalization electronic energy reduced to the lowest point for the un-matching patterns of the electron density.
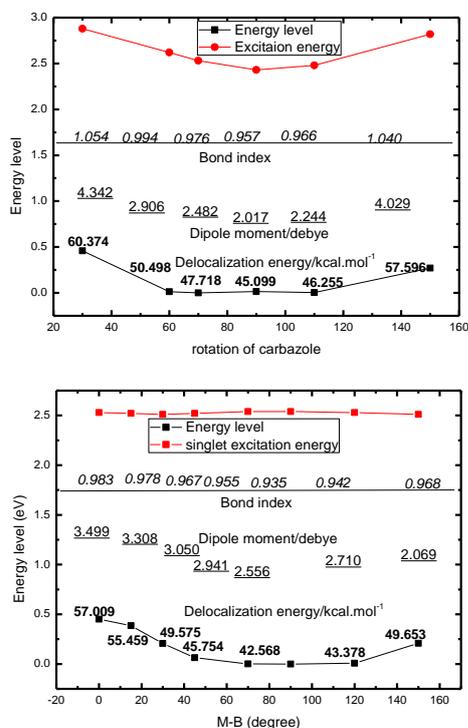
The gap of the first peak and the second peak excitation gap of carbazoly compounds is about 1.18 eV while those of diphenylamino compounds is about 1.22 eV. The gap of the S1 and T1 in coplanar structure is, the gap of vertical configuration between carbazolyl and naphthalimic ring is 0.716 eV, and the gap of global minimum structure is about 0.349 eV. However, the original structure is the vertical frank-condon structure. Whatever the vertical configuration or the coplanar configuration, they all increase the gap of S1 and T1 to some extent, thus induce the increasement of quantum yield.

For compound IV, when dihedral angle between the carbazole and naphthalimic ring is 90 degree in Fig. 5, there shows one negative imaginary frequency unexpectedly. There show two lowest points on the left and right sides, suggesting self-on and off reaction might occur. The calculation started from the lowest point along the transition state geometries. The intrinsic reaction coordinates are produced. The activation energy forward and backward between them is about 0.1675kcal.mol⁻¹ and 0.1688 kcal.mol⁻¹.



Intrinsic Reaction Coordinate=-0.20878 Total Energy(+33261.6)(eV)=-0.0270731
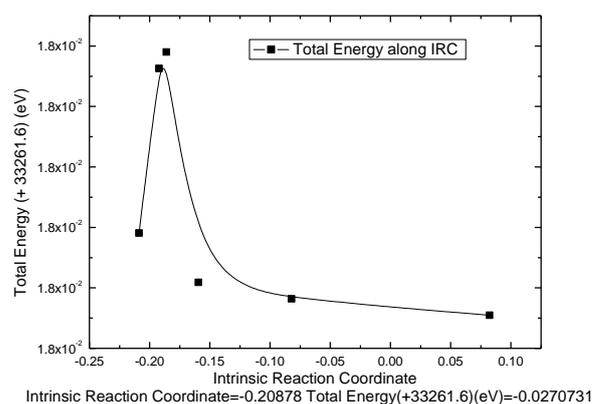
*Fig. 5. Total energy along Intrinsic reaction coordinate (IRC) curves started from the two minimum geometries for the 4-carbazolyl-N-methyl-1,8-naphthalimide*

## 4. Conclusion

The singlet excited states of 4-carbazolyl/4-diphenylamino-N-(H-, methyl, cyclohexyl, phenyl)-1,8-naphthalimide derivatives have been investigated by TDDFT model. There are three peaks in the gas phase absorption spectrum. They are consist of ICT state (the first peak), locally excited state (the second peak) and another local excited state (the third peak). Substituents on the imides have a few influences on the first peak (ICT) but can strengthen its intensity accompanied with the increased donating ability from H, methyl and chair-cyclohexyl to phenyl. The bridged diphenyl between diphenylamino and carbazolyl group made red-shift of three peaks. From $S_0$ to $S_1$, the wavelength-shift values from the configuration change of diphenylamino compounds are bigger than those of carbazolyl compounds, which made them more sensitive to the solvent. From the absence of the first emission in the case of caconical carbazolyl-naphthalimic ring and the



*Fig. 4. Rotation energy (singlet and triplet) curves as a function of twisted benzene and carbazole configuration for the 4-carbazolyl-N- phenyl-1,8-naphthalimide*

absence of the second peak in the case of planar carbazole-naphthalimic ring, it is concluded that the ICT state is more planar than the LE state, which may be connected by a global minimum at about 70°. Caconical structure of methyl carbazole is a local minimum.

### Acknowledgement

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