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RESEARCH ARTICLE

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Photochromic reactions of 6-hydroxy-5,12-naphthacenequinone and its derivatives bearing methyl or phenyl groups

Abstract Photoisomerizations of 6-hydroxy-5,12-naphthacenequinone and its derivatives bearing methyl and phenyl group were theoretically investigated with density functional theory and *ab initio* CIS method at the B3LYP 6-31G basis set, respectively. The obtained potential energy curves revealed that a four-state cycle existed in the ground and excited states. It was also found that the activation energy for the methyl transfer was higher compared to that for the phenyl transfer, and this was consistent with the experimental results that the photoisomerization of the phenyl substituted derivative was more rapid than that of the methyl substituted derivatives. Further hybrid time-dependent density functional theory (TD-DFT) was used to investigate the absorption and fluorescence spectra of these compounds under solvent effect condition. The calculated values were in agreement with the experimental results and the excitation condition of photochromic reactions.

Keywords naphthacenequinone, photochromism, photoisomerization, density functional theory, electronic spectra

Photochromic materials have great application potential in the information storage, photo transformation device, and photo switch field [1–5]. Naphthacenequinone is much more focused due to its fatigue tolerance and thermal stability [6]. Its photochemical mechanism is: under ultraviolet radiation, the 1, 5 group transfer of naphthacenequinone occurs from trans quinone to ana quinone and the latter can absorb visible light. The reversible process occurs under the visible light radiation (Fig. 1). Recently, the mainly researched naphthacenequinones are the phenyl transfer ones, and the replaced group is on the phenyl-oxygen site [7–9]. In order to know the influence of the structure on the color changing property of the compound, we have reported the influence of different transfer groups [10]. In this paper, the photochromic process of the 6-hydroxy-5,12-naphthacenequinone and its derivatives bearing methyl and phenyl group were theoretically investigated and its photochromism mechanism was further studied.

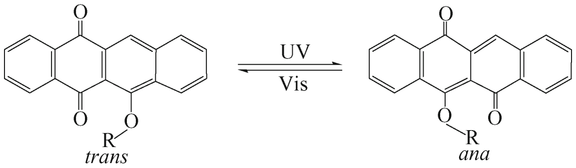

Fig. 1 Photoisomerization of the naphthacenequinone compounds

1 Calculation method

The calculation model was optimized by B3LYP/6-31G, using density functional theory (Fig. 2). The shaken analysis was utilized to confirm the stable state of the isomers and the first grade saddle-point transition state, which was further confirmed by IRC of the inner reaction. Further hybrid time-dependent density functional theory was used to calculate the absorption and fluorescence spectra of these compounds under solvent effect condition. All the calculation processes were completed on the Gaussian 03 quantum chemistry program package run on the PIV 3.0G computer.

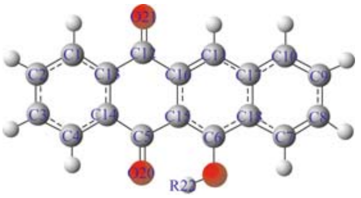

Fig. 2 Structures of the naphthacenequinone compounds

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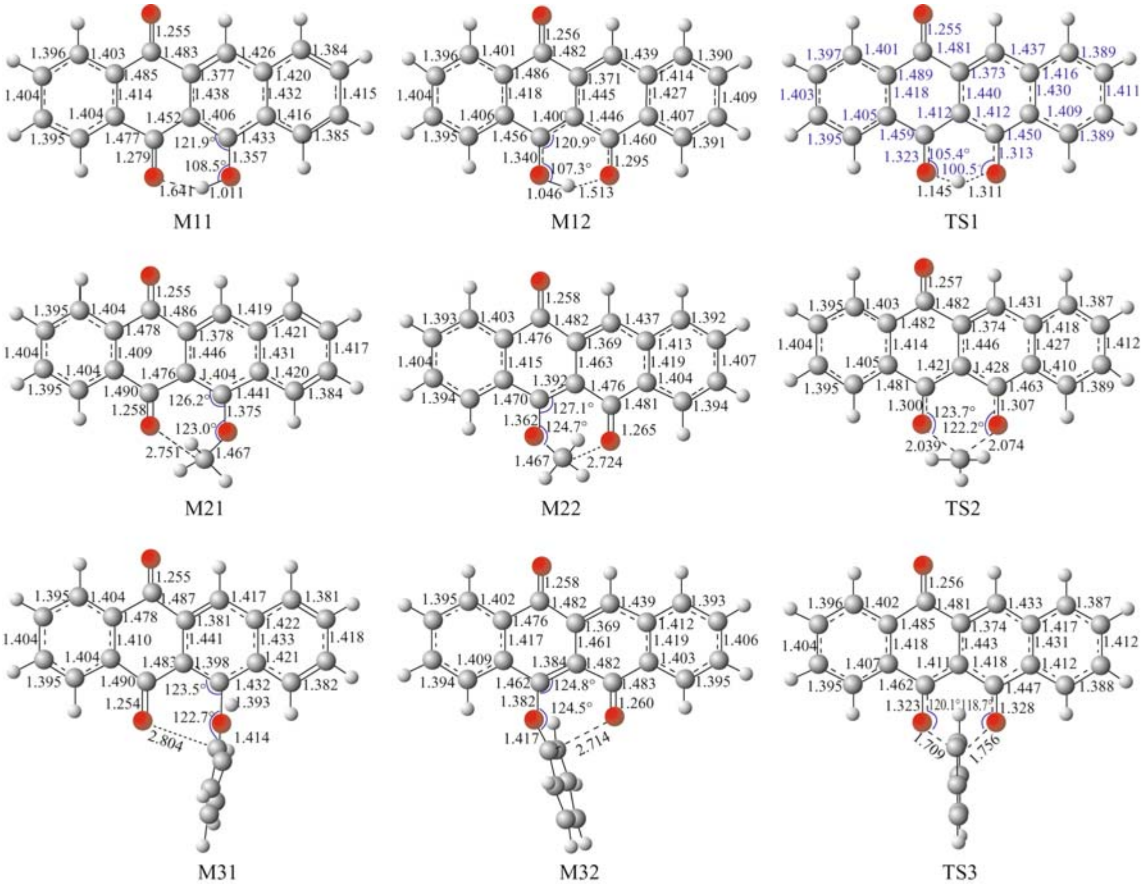
2 Result and discussion

2.1 Molecular structure

All the structures of the 6-hydroxy-5, 12-naphthacenequinone and its derivatives bearing methyl and phenyl group in the photochromism reaction are listed in Fig. 3. Parts of the bond length and angle parameters were marked in the figure. The shaken frequency calculation analyses showed that all the frequencies for the isomers were positive, indicating that the isomers can exist stably. And there was only one pseudo-frequency for each of the transitional states, indicating that it was the first grade saddle-point and the transitional states were true.

It can be seen from the structures in Fig. 3 that whether it is in ground state or excited state, the transforming trend from trans quinone to ana quinone of the three structures are always similar: the four phenyl rings are approximately in one plane. The bond length of the C(14)–C(5) and C(15)–C(5) became shorter while the C (15)–C(6) and C(18)–C(6) longer. The length of the other bonds of the four phenyl rings changed alternatively, which indicates when the isomerization occurred, the electron cloud of the C(14)–C(5) and C(15)–C(5) increased, while that of the C(15)–C(6) and C(18)–C(6) decreased.

Because of the differences of the replaced group at the position 22, the compounds M11, M21, and M31 showed different structures, respectively. The hydrogen atom at the position 22 of M11 was in the same plane with the four phenyl rings of the trans quinone and ana quinone in both ground and excited state. The length of the O(20)H(22) bond of M11 was 0.1641 nm while the length of the O(19)H(22) bond of M12 was 0.1513 nm, indicating that the trans quinone structure M11 and the ana quinone structure M12 both form an intramolecular hydrogen bond. The angle data of the O(19)–C(6)–C (15)–C(5) and O(20)–C(5)–C(14)–C(4) planes for M21 and M31 showed that the torsional angle change at the excited state from the trans quinone to ana quinone structure is much smaller than that of the ground state. The transitional structures of the ground and excited states maintain their plane structure. This result suggests that the transfer occurs more easily in the excited sate than in the ground state for the M21 and M31 compounds.



(a)

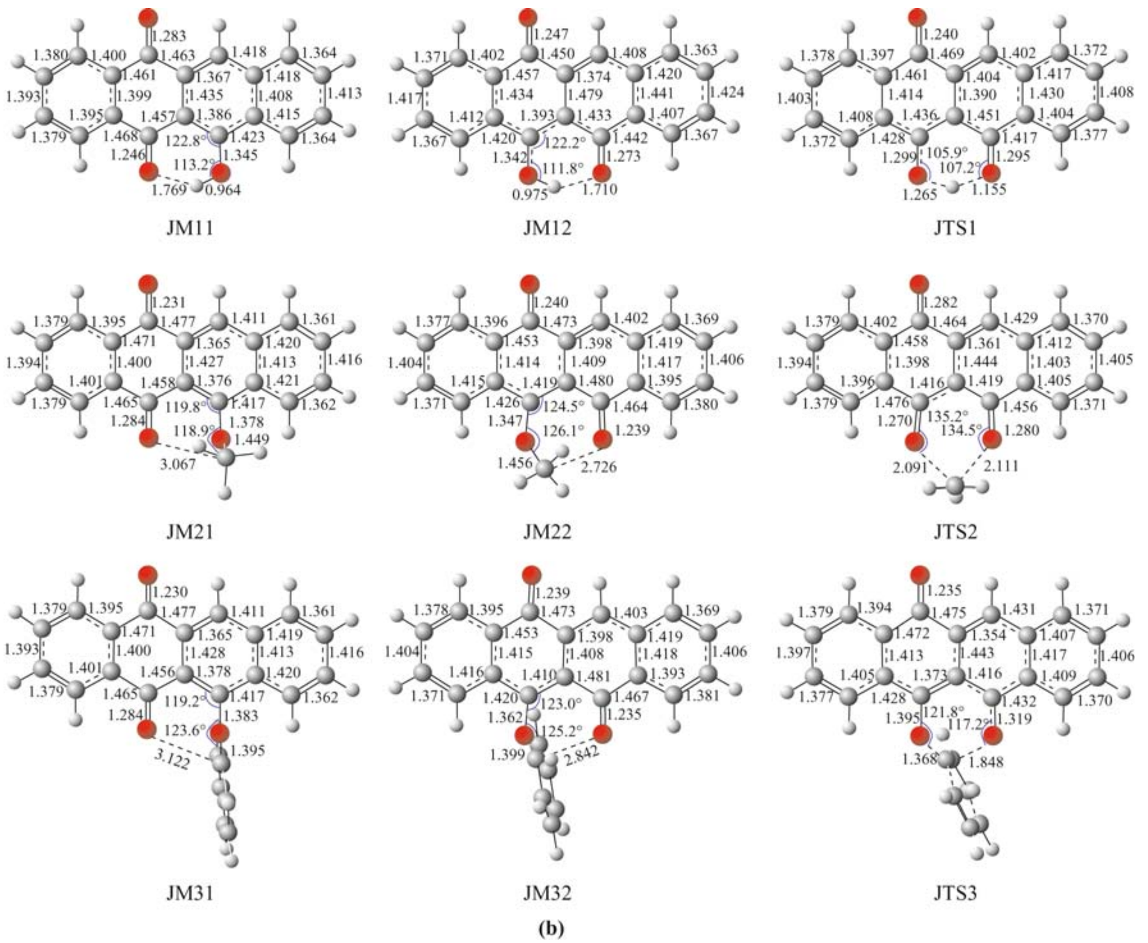


Fig. 3 Geometric structures of isomers and transition states of 6-hydroxy-5,12-naphthacenequinone and its substitutive derivatives in the ground state (a) and excited state (b) (bond distances are in Å and angles in degree)

2.2 Isomerization reaction

2.2.1 The solvent effect

In order to reveal the actual condition of the molecules in the solvent, the solvent effect was considered in the calculation process. There are many factors influencing the quinone compounds, including the polarization effect, the proton effect and the aromaticity effect. But the main factor is the strength of the polarization of the solvent [11]. The optimization of the 6-hydroxy-5, 12-naphthacenequinone was made by the B3LYP/6-31G method for gas phase and in dimethyl sulfoxide condition, as shown in Table 1. When considering the solvent effect, the activation energy for the reaction and its reversible reactions was 183.2 and 155.5 kJ/mol, respectively, indicating that the isomerization process absorbed 27.7 kJ/mol. In the gas phase condition, the energy was 184.1 and 155.9 kJ/mol, respectively, indicating absorbance of 29.2 kJ/mol in the process, which barely changed compared to that in the solvent condition. The UV-visible absorb spectra were also calculated on the optimization basis and the wavelength only red-shifted for 7 nm. The solvent dimethyl sulfoxide has little effect on the activation energy of the compound, indicating that the static field created by dimethyl sulfoxide has little influence on the molecular system.

2.2.2 Isomerization reaction

B3LYP and ab initio HF methods were used to optimize the structure of the isomers of the 6-hydroxy-5, 12-naphthacenequinone. The zero point energy, total energy, and shaken frequency are listed in Table 1. Comparing the results of the DFT/B3LYP and the HF method, it was found that the corresponding energy sequence of the ground state, excited state, and transitional state did not change. The results obtained by the two methods were the same.

The isomerization energy profile is shown in Fig. 4. We can see from Fig. 4 that the M11 and M12 are not stable to heat. At room temperature, their trans quinone and ana quinone isomers can interchange instantaneously, and this is related with the intramolecule H bond, the formation of which can lower the activation energy for isomerization greatly.

Table 1 Zero-point energies *E*zp, total energies *E* and vibration frequencies of the isomers and transition states of 6-methoxy-5,12-naphthacenequinone and its substitutive derivatives in the ground and excited state

species	B3LYP (no solvent)			B3LYP (dimethyl sulfoxide)			HF (no solvent)			CIS (no solvent)		
	E_{zp}/(a.u.)	E/(a.u.)	v/cm^{-1}	E_{zp}/(a.u.)	E/(a.u.)	v/cm^{-1}	E_{zp}/(a.u.)	E/(a.u.)	v/cm^{-1}	E_{zp}/(a.u.)	E/(a.u.)	v/cm^{-1}
M11	0.234354	−917.421033	–				0.252680	−911.492680	–	0.249915	−911.738768	–
M12	0.233291	−917.413939	–				0.252495	−911.479982	–	0.249978	−911.720804	–
TS1	0.230289	−917.413379	834.1i				0.247600	−911.475573	1744.6i	0.244809	−911.714821	1530.7i
M21	0.261956	−956.423456	–	0.260187	−956.442925		0.281632	−950.444446	–	0.279279	−950.295322	–
M22	0.261981	−956.412351	–	0.260280	−956.432365		0.281809	−950.427695	–	0.279101	−950.300020	–
TS2	0.259204	−956.353348	583.6i	0.257406	−956.373153	572.6i	0.278048	−950.352260	663.9i	0.275369	−950.199218	662.5i
M31	0.314936	−1148.070333	–				0.338941	−1140.838164	–	0.336692	−1140.690748	–
M32	0.314734	−1148.056796	–				0.338738	−1140.819749	–	0.336208	−1140.692599	–
TS3	0.312804	−1148.014321	518.3i				0.336046	−1140.747534	763.8i	0.336200	−1140.665491	350.1i

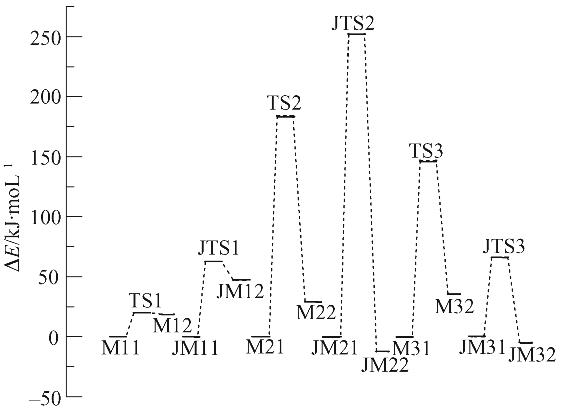


Fig. 4 Schematic diagram of potential energy surfaces describing isomerization reactions with the energy of 6-hydroxy-5, 12- naphthacenequinone taken as zero point

In addition, when the M11 isomerizes to M12, whether in ground state or in excited state, the trans quinone is more stable than the ana quinone. When the M21 and M31 isomerize to M22 and M32, the trans quinone is more stable than the ana quinone in ground state. But when excited to the first level, the ana quinone is more stable than the trans quinone, indicating that the M21 and M31 can form a four-energy level reaction. But due to high isomerization activation energy, the whole reactions cannot cycle. That is to say, it is difficult for the isomerization reaction to happen either in the ground state or in the excited state for the M21 compound, and this agrees well with our result that the photochromism property of M21 is bad [10].

Comparing the transitional state energy of the three compounds bearing different groups at position 22, we found the energy sequence is as follow: CH3, C6H5 and H derivatives. Figure 5 is the HOMO electron cloud distribution of the M11, M21 and M31. The oxygen atom in the mixed alkyl-aryl ether of M21 seems to have a sp2 hybrid orbit. And the lone pair electrons of the p orbit of oxygen atom parallel with that of π electron orbit in the phenyl rings, forming a delocalization π bond. This conjugation effect shortens the C(6) and O(19) bond to 0.1375 nm and strengthens the stability. However, the electron cloud distribution figure of M31 shows that the lone pair electrons of the p orbit of oxygen atom is perpendicular to the plane of π electron orbit in the phenyl rings of naphthacenequinone, and the bond length of the C(6) and O(19) is 0.1393 nm, lowering the conjugation effect. So, the stability of M31 is lower than that of M21. The transitional state destroys such a stable condition and the isomerization energy from M21 to M22 rises up and the energy from M31 to M32 goes down. Although the electron cloud distribution figure of M11 shows a rigid conjugation structure, the hydrogen bond between the H(22) and O(20) lowers the photoisomerization activation energy greatly and so the transitional state energy is the smallest.

The forward and backward activation energy of M21 and M31 are both higher than that of the M11, and this makes the ana quinone structure of M21 and M31 more stable. However, the forward and backward activation energy of M31 is smaller than that of M21, thus stabilizing the ana quinone structure of M31 and facilitating the transfer from trans quinone to ana quinone at the same time. This well explained our experimental results that the η value of quinone isomer is: $\eta(\mathrm{M21}) = 0.42$;

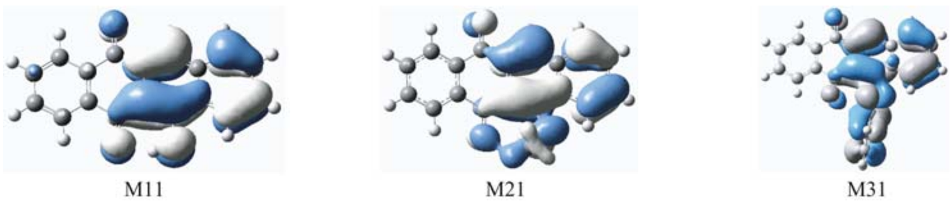


Fig. 5 HOMO electron cloud distribution of M11, M21 and M31

η(M31) = 1.77; where η = Aa/At, Aa stands for the maximum value at the maximum absorb-wavelength of ana quinone structure while At stands for that of trans quinone. The chromism property of M21, where the transfer group is methyl, is worse than that of the M31, where the transfer group is phenyl.

IRC is usually used to estimate if the transitional state is the real one, i.e., if the transitional state is correctly connected to the reactants and products. The changes of atomic distance and dihedral angle of the key sites for M11 along the reaction axis are shown in Fig. 6. IRC calculation results for TS1 confirmed that the transitional state was the real one connecting the reactant M11 and product M12. The whole reaction process was the breakup of O (19)–H (22) bond and the formation of O(20)–H(22) bond. Dihedral angles (19)_C(6)–C(15)–C(5) and O(20)–C(5)–C(14)–C(4) nearly equal zero. The transitional state has a six-membered ring structure suggesting that the six atoms are always in the same pseudo-plane in the reaction. The transfer of H (22) from O (19) to O(20) was a typical transfer in the same plane.

The transitional state has also been confirmed by the coordinate's calculation of M21 and M31 in the intrinsic reaction, and the results are the same as described above.

2.3 Electronic spectra

2.3.1 UV absorbance spectra

TD/DFT was used to calculate the UV absorbance spectra, the results are shown in Table 2. The experimental spectra of M21 agreed well with the theoretical spectra. The calculated result showed that the maximum absorbance peak of trans quinone was located in the UV area, while the peak of ana quinone was in visible light area, both of which suited with their radiation excitation conditions. The UV radiation can stabilize the compound to photo-stable state of chromism and the visible light radiation can stabilize the compound to photo-stable state of achromism.

The electron transfer is produced by interaction between the dipole moment change of the atoms or molecules and the electromagnetic field of the light wave. This kind of transition is called electronic dipole transition or magnetic dipole transition. The energy levels can be attained by solving Schrodinger equation with time variables. This state-state transition probability is defined by the transition moment of the electronic dipole moment. The spectra data in Table 2 show that the orbit overlap of M22 reached maximum value when the transition took place from HOMO to LUMO.

Frontier molecular orbital graphs of maximum contribution to transition corresponding to $\lambda_{\max}$ in M22 are shown in Fig. 7. The maximum contribution to transition came from HOMO to LUMO. The maximum transition of ana quinone corresponded to the charge transfer taking place between the phenyldiquinone and phenyl rings. The electron cloud distribution of methoxy had little change.

Frontier molecular orbital graphs of maximum contribution to transition corresponding to $\lambda_{\max}$ in M31 are shown in Fig. 8. The maximum contribution to transition came from HOMO-1 to LUMO. The maximum transition of trans quinone corresponded to the charge transfer taking place between the substituted phenyl ring and the phenyldiquinone. After the transfer, the charges distributed on the whole phenyl ring.

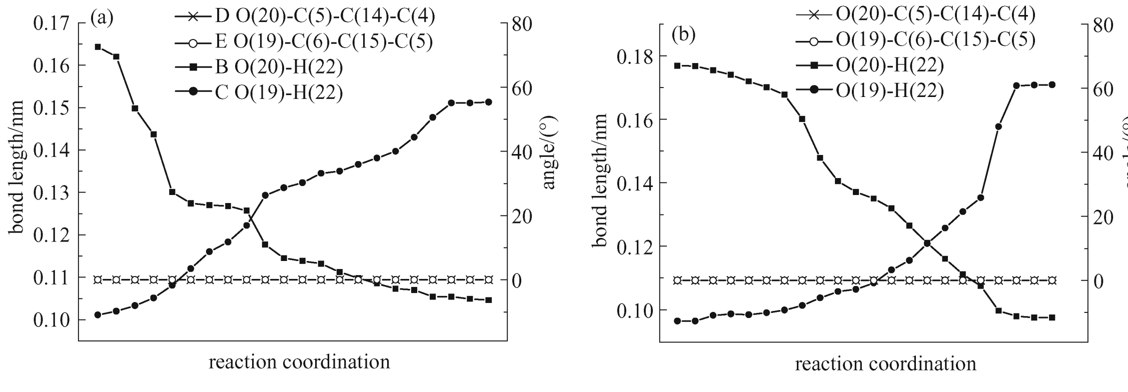


Fig. 6 Variation of geometric configuration parameters of M11 → M12(a) and JM11 → JM12(b) during isomerization process

Table 2 Ultraviolet spectroscopy data of M21 and M31 in DMSO solution

	λ_{calcd}/nm	f	transition energy/eV	transition nature	coefficient	λ_{exp}/nm
M21 (*trans*)	290.97	0.5885	4.2611	HOMO-1 → LUMO + 1	0.58927	284
M22 (*ana*)	502.45	0.4466	2.7501	HOMO → LUMO	0.62530	501
M31 (*trans*)	418.13	0.1388	2.9652	HOMO-1 → LUMO	0.57613	395
M32 (*ana*)	471.32	0.1196	2.6306	HOMO-2 → LUMO	0.48105	473
	412.88	0.0056	3.0029	HOMO-2 → LUMO + 1	0.18018	418

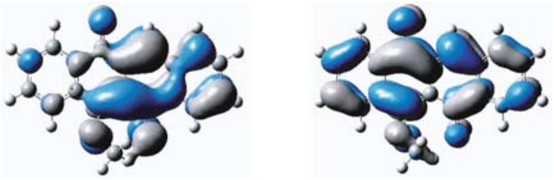


Fig. 7 Frontier molecular orbital graphs of maximum contribution to transition corresponding to λ_{max} in M22

Fig. 8 Frontier molecular orbital graphs of maximum contribution to transition corresponding to λ_{max} in M31

Table 3 Fluorescence spectroscopy data of JM21 and JM31 monomers in THF solution

	λ_{calcd}/nm	f	transition energy/eV	transition nature	coefficient	λ_{exp}/nm
JM21 (*trans*)	425.97	0.2356	2.9106	HOMO → LUMO	0.64705	458
JM22 (*ana*)	566.21	0.4529	2.1897	HOMO → LUMO	0.59852	
JM31 (*trans*)	412.08	0.2072	3.0087	HOMO-1 → LUMO	0.63218	
JM32 (*ana*)	579.16	0.3418	2.1408	HOMO → LUMO	0.56989	

2.3.2 Fluorescent spectra

TD/DFT was used to calculate the fluorescent spectra; the results are shown in Table 2. The maximum absorbance spectra of M21 are near to the experimental spectra, indicating that the density function method is reliable for the fluorescent spectra calculation of naphthacenequinone compounds.

3 Conclusions

Energy analysis shows that the 6-hydroxy-5, 12-naphthacenequinone was unstable to heat and its derivatives bearing methyl and phenyl group were stable to heat and they had photochromism property. The experimental results theoretically explain that the chromism of M21 with transfer group of methyl is lower than that of M31 with transfer group of phenyl. In the isomerization reaction, the ground state and the excited state of M31 compound formed a four-energy-level process and the whole reaction was a cycle. When the energy of excited ana quinone structure was released as fluorescent form, it was strengthened by the cycle reaction. The maximum absorbance peak of trans quinone was located within the UV area, while the maximum absorbance peak of ana quinone was located within the visible light area, both of which suited with their radiation excitation conditions. The UV radiation can stabilize the compound to photo-stable state of chromism and the visible light radiation can stabilize the compound to photo-stable state of achromism.

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