

Theoretical Calculations of Electronic Structure and Properties of Pyrromethene Laser Dye and Related Materials

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ABSTRACT

Theoretical calculations using density functional theory (DFT) both on semi empirical and Ab initio levels have been carried out for pyrromethene laser dye and related compounds (PM-chromophore, PM-4m, PM 546, PM650 PM 567 and PM597). We carried out theoretical calculations using DFT, AM1, TD-DFT and CIS on ground and excited states for the selected laser dye materials, we obtained the optimized geometry of the molecules, UV, IR spectrum, and the transition between the ground S_0 and the first excited S_1 states exclusively, the HOMO and LUMO states and other properties.

Key words: Pyrromethene dye, Laser Dye, DFT, TD-DFT, Semi empirical, CIS, ground states, Excited states.

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Ab-initio

PM-4m, PM-chromophore

.PM597, PM567, PM 650, PM546,
CIS TD- DFT, AM1, DFT

S₀

IR UV

LOMO HOMO

S₁

CIS

1. Introduction

The photophysical properties of laser dyes have been extensively studied due to their important applications as:

- 1-Active media for tunable lasers [1,2].
- 2-Molecular probes in the characterization of biological systems [3,4].
- 3-More recently, in the design of new photo-electronic devices [5,6].

Boyer et al [7]. studied a new class of dyes, the dipyrromethene-BF₂ complexes (PM), synthesized by means of the fluoroboration of two pyrrol units linked by a methylene group.

These dyes present intense absorption and fluorescence bands in the green-red visible region and are characterized by high fluorescence quantum yields, in some cases close to the unity [3,8,9]. Furthermore, PM dyes present higher laser efficiency and photostability than rhodamine dyes [10], probably the most extensively used laser dyes. Advanced ab initio calculations for relatively “complex” molecules with more than 20 atoms in their molecular structure can be realized due to the recent improvements in quantum mechanics implemented in commercial software package. The possibility of theoretical calculations to model molecular structure with specific physicochemical properties of interest leads us to perform theoretical calculations on PM dyes. These calculations are useful to understand their photophysics, and hence to predict their lasing behavior. Moreover they could be successful tools to guide the synthesis of new PM dyes with interesting photophysical properties [11,12,13,14].

In the present work quantum mechanical calculations of pyrromethene PM laser dye at DFT -AM₁ -TD-DFT-CIS were carried out for the following five compounds:

PM-chromophore

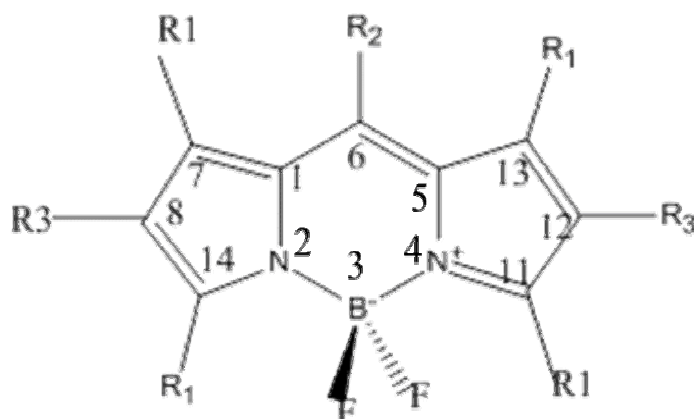
PM-4m with four methyl groups at positions 7, 11, 13, and 14

PM546 with five methyl groups at positions 6, 7, 11, 13, and 14

PM650 with six methyl groups at positions 7, 8, 13, 11, 14, and cyan at position 6

PM567 with five methyl groups at positions 6, 7, 13, 14, 11, and two ethyl groups at position 8, 12

PM597 with five methyl groups at positions 6, 7, 13, 14, 11, and two groups $C(CH_3)_3$ at position 8, 12 (see Table(1) and Fig(1)).



Fig(1) Molecular structure of the PM dye and the related compounds.

Table(1) Values of R of PM chromophore and related compounds.

Dye	R ₁	R ₂	R ₃
PM-chromophore	H	H	H
PM-4m	CH ₃	H	H
PM546	CH ₃	CH ₃	H
PM650	CH ₃	CN	CH ₃
PM567	CH ₃	CH ₃	C ₂ H ₅
PM597	CH ₃	CH ₃	C(CH ₃) ₃

The theoretical calculations were focused on:

(i) The optimization of the molecular geometry of the compounds in the ground S_0 and first excited singlet S_1 states.

(ii) The absorption and emission transitions between both states. Exclusively involves the HOMO and LUMO states.

2- Computational details

The molecules were drawn using CHEM BIO software and theoretical calculation carried out by Gaussian 03 software [15]. The optimization of the ground S_0 state geometry of PM dye was performed by DFT-B3LYP- basis set 6-31G [16,17] and semiempirical calculations (AM1).

The optimization geometry of the excited S_1 state of PM dye was performed by ab initio (CIS) [18,19]. While the absorption bands were performed by TD-DFT [20,21].

3- Results and discussion

The computation time required for DFT-B3LYP (lasts from hours to days) is drastically reduced in semiempirical calculations (minutes) in determinate of the accuracy of the theoretical calculations.

Table (2) shows some bond length of PM chromophore and related compounds for the ground S_0 state and excited S_1 state.

Table (2) Bond length of PM chromophore and related compounds Bond lengths (Å)

PM	Atoms	B3LYP/6-31G	AM1	CIS	X-ray
PM-chromophore	C(5)-C(6)	1.3923	1.3914	1.4075	
	C(1)-C(6)	1.3924	1.3914	1.4075	
	B(3)-F(10)	1.4256	1.3104	1.3508	
	B(3)-F(9)	1.4249	1.3105	1.3508	
	N(2)-C(14)	1.3519	1.3474	1.346	
	C(1)-N(2)	1.4084	1.421	1.429	
	C(12)-C(13)	1.3943	1.3935	1.3744	
PM-4m	C(7)-C(8)	1.3944	1.3935	1.3744	
	C(5)-C(6)	1.3908	1.3897	1.4059	
	C(1)-C(6)	1.3908	1.3918	1.4059	
	B(3)-F(10)	1.4372	1.3132	1.355	
	B(3)-F(9)	1.4372	1.3131	1.355	
	N(2)-C(14)	1.3608	1.3577	1.3567	
	C(1)-N(2)	1.4099	1.4189	1.4184	
PM-4m	C(12)-C(13)	1.3971	1.3945	1.3739	
	C(7)-C(8)	1.3971	1.3973	1.3739	
	C(5)-C(6)	1.4085	1.4038	1.4228	1.394
	C(1)-C(6)	1.4083	1.4039	1.4229	1.398
	B(3)-F(10)	1.4389	1.315	1.3545	1.394
	B(3)-F(9)	1.4398	1.3155	1.3583	1.394
	N(2)-C(14)	1.3596	1.3569	1.3553	1.342
PM650	C(1)-N(2)	1.4135	1.4196	1.4211	1.401
	C(12)-C(13)	1.398	1.398	1.3748	1.373
	C(7)-C(8)	1.3977	1.398	1.3748	1.380
	C(5)-C(6)	1.4062	1.3989	1.4247	
	C(1)-C(6)	1.4062	1.3988	1.4247	
	B(3)-F(10)	1.4371	1.3132	1.3533	
	B(3)-F(9)	1.4371	1.3131	1.3565	
PM567	N(2)-C(14)	1.3604	1.3554	1.3514	
	C(1)-N(2)	1.4039	1.4193	1.4191	
	C(12)-C(13)	1.4032	1.3988	1.3811	
	C(7)-C(8)	1.4032	1.3986	1.3811	
	C(5)-C(6)	1.4096	1.404		
	C(1)-C(6)	1.4092	1.4041		
	B(3)-F(10)	1.4402	1.3157		
PM567	B(3)-F(9)	1.441	1.3149		
	N(2)-C(14)	1.3589	1.356		
	C(1)-N(2)	1.4098	1.4188		
	C(12)-C(13)	1.4071	1.4023		
	C(7)-C(8)	1.4065	1.4024		

Theoretical calculations show no difference between bond length which were calculated by DFT for PM-chromophore compared with that for PM-4m by the same method. There was an increase in the bond length especially (C1-C6), (C5-C6) in all compounds due to the methyl group at position 6 in PM546 and PM 567 and cyanide group at the same position.

Table. (3) shows bond angles of PM chromophore and related compounds for the ground S_0 state and excited S_1 state.

Table(3) Bond angles of PM chromophore and related compounds. Bond angles($^{\circ}$)

PM	Atoms	B3LYP/6-31G	AM1	CIS	X-ray
PM-chromophor	H(21)-C(14)-N(2)	120.9532	122.3722	121.1398	
	H(20)-C(13)-C(5)	125.3448	124.6257	124.672	
	H(18)-C(11)-N(4)	120.9491	122.3782	121.1394	
	H(16)-C(7)-C(1)	125.338	124.6317	124.6723	
	F(10)-B(3)-F(9)	109.6265	107.9258	114.2024	
	B(3)-N(2)-C(1)	125.4263	124.6954	127.7251	
PM-4m	N(4)-B(3)-N(2)	106.546	105.8758	102.0831	
	C(17)-C(14)-N(2)	122.4021	125.5892	122.256	
	C(15)-C(13)-C(5)	126.2394	125.1248	125.0681	
	C(18)-C(11)-N(4)	122.4018	126.362	122.2553	
	C(16)-C(7)-C(1)	126.2391	125.9306	125.0672	
	F(10)-B(3)-F(9)	108.4666	107.5164	113.6378	
PM546	B(3)-N(2)-C(1)	124.9288	124.5991	127.1215	
	N(4)-B(3)-N(2)	107.4507	106.3491	102.9422	
	C(19)-C(14)-N(2)	122.749	126.3932	122.6276	
	C(16)-C(13)-C(5)	129.763	128.1451	128.4179	
	C(15)-C(11)-N(4)	122.7184	126.3917	122.6271	
	C(18)-C(7)-C(1)	129.9506	128.1458	128.4155	
PM650	F(10)-B(3)-F(9)	108.239	107.0912	113.5301	
	B(3)-N(2)-C(1)	125.686	125.0444	126.9199	124.9
	N(4)-B(3)-N(2)	107.2918	105.9692	102.3108	108.0
	C(17)-C(14)-N(2)	122.0815	126.0776	122.2956	
	C(16)-C(13)-C(5)	126.7212	126.2463	125.7196	
	C(15)-C(11)-N(4)	122.0809	126.0391	122.295	
PM567	C(18)-C(7)-C(1)	126.7206	126.1354	125.7176	
	F(10)-B(3)-F(9)	108.4768	107.4426	113.6553	
	B(3)-N(2)-C(1)	125.7832	124.9449	127.3907	
	N(4)-B(3)-N(2)	107.2901	106.1962	102.6786	
	C(19)-C(14)-N(2)	121.8934	126.0949		
	C(16)-C(13)-C(5)	128.5636	127.5884		
	C(15)-C(11)-N(4)	121.8356	126.0949		
	C(18)-C(7)-C(1)	128.5656	127.5894		
	F(10)-B(3)-F(9)	108.1784	107.0965		
	C(14)-N(2)-C(1)	109.3023	108.9597		
	N(4)-B(3)-N(2)	107.3994	106.0286		

There was an increase in the bond angles for ($C_5-C_{13}-C(x)$) due to the methyl group at the position 6 or CN group at the same position about 3°.

Table (4) shows Dihedral angles of PM chromophore and related compounds for the ground S_0 state and excited S_1 state

Table (4) Dihedral angles of PM chromophore and related compounds
Dihedral angles(°)

PM	Atoms	B3LYP/6-31G	AM1	CIS	X-ray
PM-chromophore	C(11)-C(12)-C(13)-C(5)	0.0092	0.0051	-0.0053	
	N(4)-C(5)-C(6)-C(1)	0.1319	0.0122	0.0642	
	C(13)-C(5)-C(6)-C(1)	-179.3654	-179.978	-179.923	
	C(13)-C(5)-C(6)-H(15)	0.4258	-0.0105	0.0221	
	N(2)-B(3)-N(4)-C(5)	-1.904	-0.029	-0.073	
	F(9)-B(3)-N(4)-C(11)	59.308	59.8718	63.2284	
PM-4m	C(7)-C(1)-C(6)-H(15)	-0.4141	0.0415	-0.0126	
	C(14)-N(2)-B(3)-F(9)	-59.3284	-59.8198	-63.2403	
	C(11)-C(12)-C(13)-C(5)	0.0742	0.008	0.0011	
	N(4)-C(5)-C(6)-C(1)	-0.1417	-0.0145	-0.0125	
	C(13)-C(5)-C(6)-C(1)	-179.9917	179.9808	179.9841	
	C(13)-C(5)-C(6)-H(19)	0.0078	0.0156	-0.0045	
PM546	N(2)-B(3)-N(4)-C(5)	-0.1465	0.0068	0.0187	
	F(9)-B(3)-N(4)-C(11)	59.8687	59.562	62.9214	
	C(14)-N(2)-B(3)-F(9)	-59.8397	-59.6516	-62.9208	
	C(11)-C(12)-C(13)-C(5)	0.0389	-0.043	-0.5212	0
	N(4)-C(5)-C(6)-C(1)	2.222	5.3214	12.716	
	C(13)-C(5)-C(6)-C(1)	-176.7364	-173.266	-165.33	180
PM650	C(13)-C(5)-C(6)-C(17)	2.818	7.2028	12.2912	
	N(2)-B(3)-N(4)-C(5)	-2.8239	-6.8895	-16.1904	0
	F(9)-B(3)-N(4)-C(11)	57.6189	54.0807	50.9246	
	C(14)-N(2)-B(3)-F(9)	-57.5752	-54.1006	-50.9466	
	C(11)-C(12)-C(13)-C(5)	0.0072	0.0071	-0.2022	
	N(4)-C(5)-C(6)-C(1)	-0.0179	0.0427	4.3716	
PM650	N(4)-C(5)-C(6)-C(1)	-0.0179	0.0427	4.3716	
	N(4)-C(5)-C(6)-C(1)	-0.0179	0.0427	4.3716	
	N(2)-B(3)-N(4)-C(5)	-0.0226	-0.191	-12.7446	
	F(9)-B(3)-N(4)-C(11)	59.9251	59.5009	55.5903	
	C(7)-C(1)-C(6)-C(19)	-0.0215	-0.0537	-4.8114	
	C(14)-N(2)-B(3)-F(9)	-59.842	-59.4932	-55.5894	
PM650	C(11)-C(12)-C(13)-C(5)	0.2122	0.1428		
	N(4)-C(5)-C(6)-C(1)	3.0474	-5.9497		
	C(13)-C(5)-C(6)-C(1)	-176.0179	172.9615		
	C(13)-C(5)-C(6)-C(17)	4.2024	-7.937		
	N(2)-B(3)-N(4)-C(5)	-3.591	6.2787		
	F(9)-B(3)-N(4)-C(11)	57.5096	64.3702		
PM657	C(7)-C(1)-C(6)-C(17)	-4.4761	7.9265		
	C(14)-N(2)-B(3)-F(9)	-56.9617	-64.3561		

The calculated dihedral angles of PM indicate that there is a loss of planarity of its π -system. This is reflected mainly in the dihedral angles between the two pyrrol rings (C13–C5–C6–C1) and in those involving the B-atom; while both pyrrol rings are nearly planar. There was decrease in the bond length B3-F9, B3-F10 between S_1 and S_0 , the geometrical parameters of PM546 calculated by different methods were compared with X-ray [22].

The results show that the DFT method was more accurate than the AM1 method.

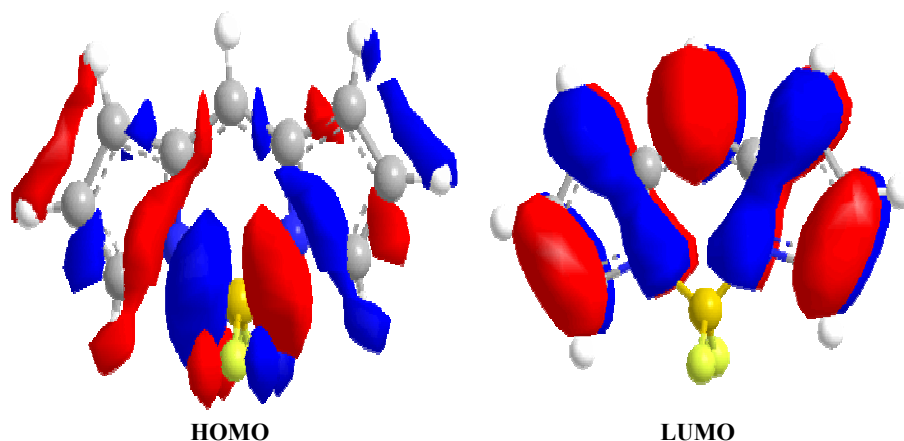


Fig (3-1) PM-chromofore

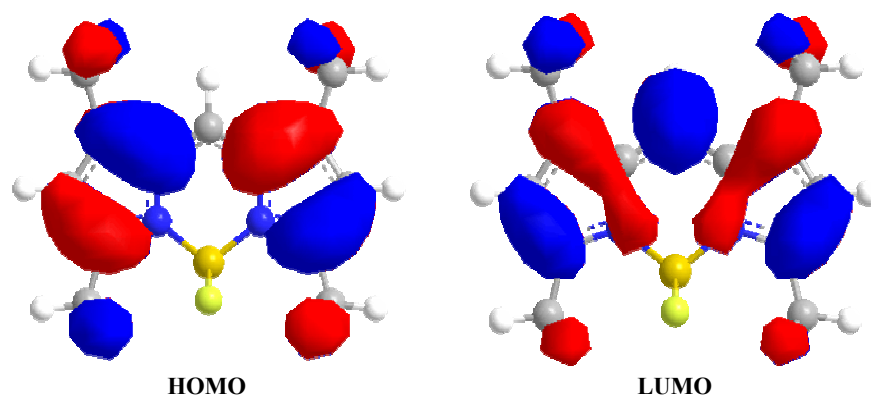


Fig (3-2) P-4M

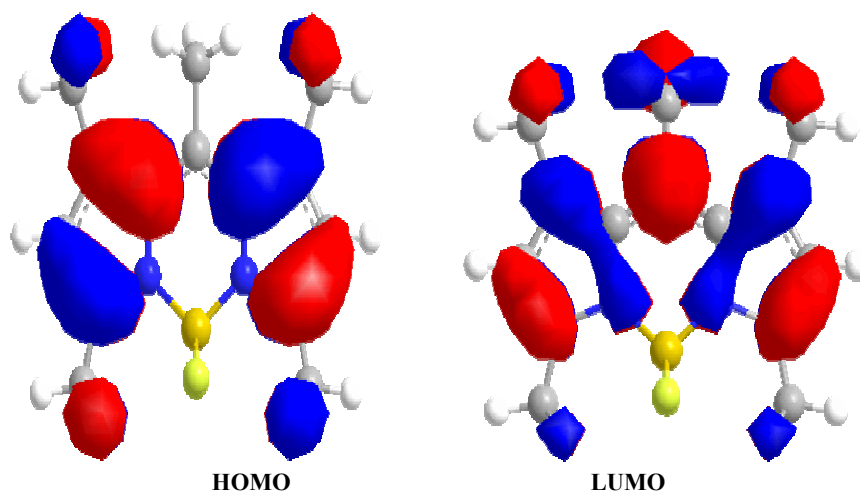


Fig (3-3) PM546

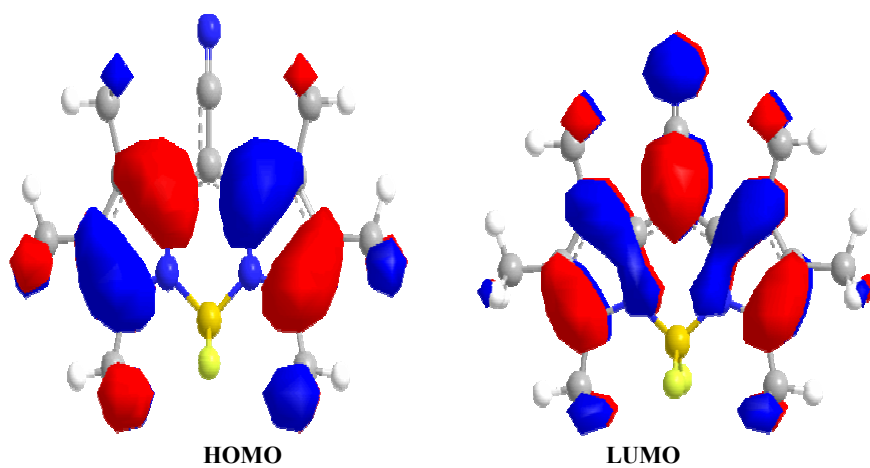


Fig (3-4) PM650

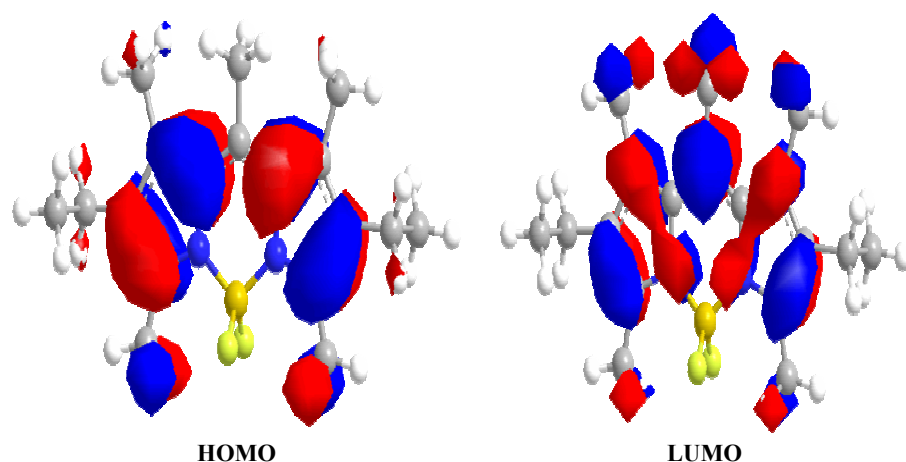


Fig (3-5) PM567

Figures: 3 (1,2,3,4,5) show the calculated contour maps of the electronic density in the HOMO and LUMO states of PM calculated by the B3LYP/6-31G method.

There was important augmentation of the electronic density in the central C6 atom.

Table (5) The calculation of energy gap ΔE , dipole moment μ and SCF

PM	$\Delta E(\text{ev})/\text{TD-DFT}$	$\mu_{S_0} \text{ D}$	$\mu_{S_1} \text{ D}$	$\Delta\mu \text{ D}$	SCF $S_0 \text{ A.U}$	SCF $S_1 \text{ a.u}$	$\Delta\text{SCF} \text{ A.U}$
PM-chromophore	3.21	5.0482	3.6134	1.44	-681.21	-668.78	12.43
PM-4m	2.96	4.5655	3.355	1.21	-838.5	-823.1	15.33
PM 546	3.03	5.1491	3.9612	1.18	-877.76	-861.7	16.06
PM650	2.45	0.3713	0.6683	-0.29	-1009.28	-990.84	18.44
PM 567	3.21	4.9282	-	-	-1034.98	-	-
PM597	3.33	-	-	-	-	-	-

The smallest energy gap was for PM650 on the other hand there was an increase in the dipole moment from S_0 to S_1 for PM650 Table (5).

Table (5) show energy gap for PM546 3.03ev where in similar theoretical calculation (TD-DFT-B3LYP/6-31G) was 3.51 and in experimental was 2.48ev that is because theoretical calculation suppose that Molecule is in isolated gas phase condition whereas experimental was by using solvents [23-24].

Table (6) The calculated excited energies, transition, and composition of the S₁ state for PM in acetonitrile at the TDB3LYP/6-31G level.

PM	Transition	Composition	Excited Energy (ev)
PM-chromophore	HOMO→LUMO	49→50	2.961
PM-4m	HOMO→LUMO	65→66	2.960
PM 546	HOMO→LUMO	69→70	2.984
PM650	HOMO→LUMO	79→80	2.344
PM 567	HOMO→LUMO	85→86	2.0984
PM597	HOMO→LUMO	101→102	3.0503

Table (6) shows the transition form HOMO to LUMO with composition and excited energy.

Table (7) The calculation of oscillator strength and absorption bands of PM by TD-DFT-B3LYP /6-31G exp[23].

PM	λ_{1ab} nm	λ_{1ab} nm (exp) [23]	λ_{2ab} nm	λ_{3ab} nm	f
PM-Chromophore	418.73		373.77	317.76	0.3033
PM-4m	418.78		385.24	312.97	0.3582
PM546	415.28	494	318.48	304.38	0.3709
PM650	528.82	590	459.8	385.75	0.3512
PM567	388.07	518	294.43	291.19	0.569
PM697	406.46	524	35.16	314.1	0.5099

Table (7) shows that the biggest values for absorption band was for PM650 whereas the biggest value for oscillator strength was for PM 697.

Table (8) The calculation of Frequenc, Deg Freedom and IR -intensity for PM TD-DFT-B3LYP/6-31G.

PM	Deg /Freedom	Frequency cm ⁻¹	IR -intensity
PM-chromophore	57	1695	486
PM-4m	93	1690	614
PM 546	102	1718	593
PM650	114	1528	434
PM 567	138	1966	1176

Table (8) shows Deg Freedom, Frequency and IR –intensity for PM546 where the largest value of frequency for IR –SPECTRUM was at 1718 cm^{-1} which include the bonds of C_6 with methyl group .

For HOMO and LUMO the electronic density was higher in the LUMO than in the HOMO at C_6 fig(3-3) and the biggest change in the bond-length for chromophore PM546 is in C_1-C_6 and C_5-C_6 .(table 2).

4-Conclusion

Theoretical calculations which were used in this work can adequately explain the geometry and the photophysical behavior of PM dyes and they can be considered as powerful tools to be applied in the design of new PM laser dyes with specific absorption and fluorescence characteristics. The DFT method gives more reliable description of the molecular geometry of PM than AM1.

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