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## **THEORETICAL DESIGNING FOR SMART MATERIALS DEVELOPMENT**

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### **Abstract**

A smart system can be considered as a design philosophy that emphasizes predictability, adaptability and repeatability. In this pursuit, the role of theoretical chemistry in the design of molecular assembly for optimum performance, and also explaining unusual function is well-recognized. To this end, our group has been extensively using DFT calculations, especially with materials that use Photoinduced Electron Transfer (PET) process to execute the defined function. This involves theoretical designing of efficient electron donors/acceptors by calculations of FMO energy differences, donor-acceptor distance, changes in Mulliken charge distribution accompanying non-covalent interactions, as well as molecular distortion. Using this approach we have been able to (i) design new photochemically stable pyromethene laser dyes that are of wide application in advanced technologies, (ii) rationalize the behavior of some porphyrins and saturated  $\beta$ -diketones in sensing metal ions of physiological relevance, and (iii) formulated noncovalently bonded supramolecular assemblies as potential energy-harvesting systems. The performances of some of these newly designed systems have also been verified experimentally.

### **1. Introduction**

Smart systems and smart materials are a new emerging materials system which combines contemporary materials science with information science. The system uses the functional properties of advanced materials to achieve high performances with capabilities of recognition, discrimination, and response to a change of its environment. The components of the entire system are integrated to perform a self-controlled smart action, similar to a living creature who can "think", make judgment and take actions.

Thus designing smart material without investment of any sort of chemicals and hazards is the greenest way to produce a cost effective mechanism. In this article this technique is explained with few published works.

### Theory as tool

Scientific groups are working in the field of designing the organic molecule that can discriminate as well as select other suitable molecules or ions interact through electron donor acceptor mechanism (EDA) or Photoinduced electron transfer (PET) or intra or intermolecular charge transfer (ICT) mechanism [1-4]. All these mechanism are well known photosynthetic mechanism.

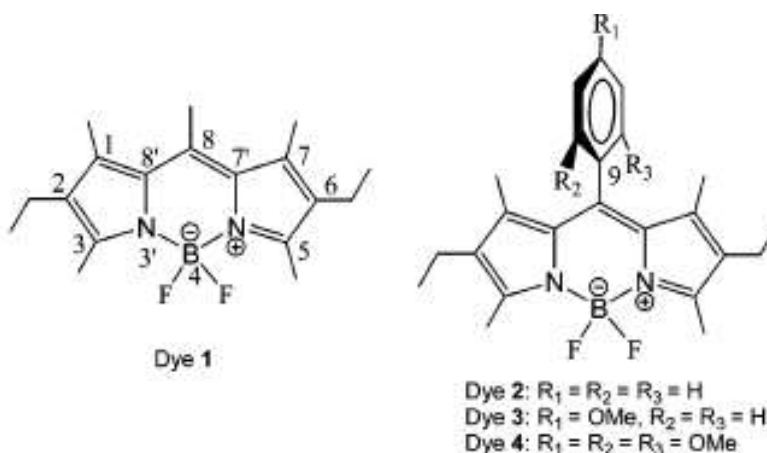
And here in these work we are using not only Molecular mechanics or DFT based theory to predict the molecular functionality or shape, but also we are verifying our theoretical prediction through spectroscopic experimentation or sometime through electrochemical checking, <sup>1</sup>H NMR study etc.

The theoretical designing covers multiple dimensions viz.

1. Functionality required to sense the target moiety.
2. In non-covalent association, molecular distortions are measured.
3. Change in Mulicken charge density if any signifies CT interaction
4. Any sort of interaction signifies beautifully by FMO orientation.
5. And the experimentally observable ground state properties like absorption parameter, NMR chemical shift etc can also be predicted computationally.

## 2. Results and discussion

### Prediction of Lasing efficiency of Pyromethene (PM) dyes:



**Figure 1:** Pyromethene dyes (PM) used for lasing efficiency study.

Analysis of the Mulliken charge distribution (Table 4) over the atoms of the PM chromophore unit did not show much variation in the electron densities at different atoms, except at C-9. Changing of the C-8 methyl substituent of **1** to the phenyl group led to an abrupt decrease in the electron density at C-9 in **2**. This was however, compensated by gradual introduction of the electron donating OMe groups in the dyes **3** and **4**. The change in electron density at C-9 appeared to have correlation with the change in broad band lasing efficiency of the PM dyes. The boron atom plays a crucial role in bridging the two pyrromethene units in the PM dyes, ensuring extended conjugation that is essential for their lasing property. The Lewis acidity of boron coupled with its size compatibility with the pyrrole nitrogen atoms is responsible for this. Evidently, a higher electron density at C-9 in **4**, as found in our theoretical calculations would facilitate the extended conjugation explaining its superior lasing efficiency.

Small change in dipole moment shown in Table 2 between S0 and S1 states indicates weak solvatochromism of the PM dyes. A well as higher dipole moments signifies better polarizability & higher lasing efficiency.

**Table 1:** Net charges (Mulliken) on different atoms of the dyes **1-4** at their respective optimized ground state geometries, calculated by *ab initio* HartreeFock (6-31G\*\*) )

Dye	C-1	C-2	C-3	N-3'	B-4	C-8	C-8'	C-9
dye <b>1</b>	+0.03	-0.15	+0.35	-0.80	+1.13	+0.08	+0.18	-0.35
dye <b>2</b>	+0.03	-0.16	+0.36	-0.80	+1.13	+0.02	+0.21	-0.06
dye <b>3</b>	+0.03	-0.16	+0.37	-0.81	+1.15	+0.02	+0.21	-0.09
dye <b>4</b>	+0.05	-0.17	+0.37	-0.82	+1.16	+0.05	+0.22	-0.20

**Table 2:** Ab initio calculated molecular parameters of the dyes **1-4**.

molecular paramaters	Dye <b>1</b>	Dye <b>2</b>	Dye <b>3</b>	Dye <b>4</b>
E-HOMO (eV)	-6.8022	-6.7374	-6.7158	-6.7123
E-LUMO (eV)	+1.0171	+1.0005	+0.9988	+0.9468
Band Gap(eV)	+7.8193	+7.7379	+7.7145	+7.6590
$\mu_0$ (Debye)	+4.5544	+4.8522	+5.8935	+5.0115
$\mu$ (S <sub>1</sub> , Debye)	+4.5750	+4.9276	+5.9608	+5.0260

Thus theoretical designing predicts dye **4** will be of higher lasing efficiency than the other three PM dyes. Experimental findings justified this theoretical prediction was already reported by Mula *et al.* [5].

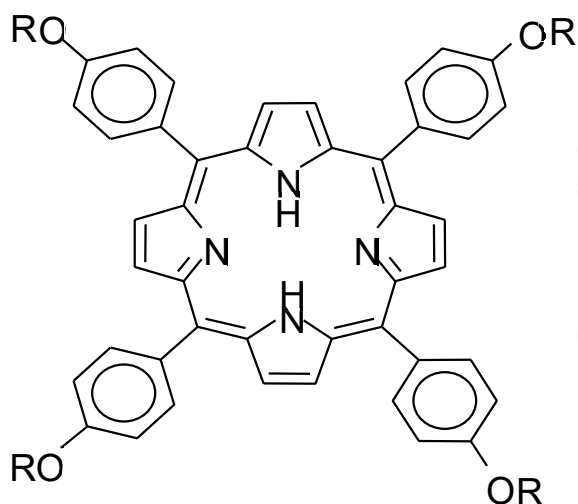
### Molecular selectivity prediction: Fullerene can act as donor

We all know that porphyrin-fullerene systems are well known assembly largely used in energy conservation purpose. Here we are showing that how does 60-fullerene can discriminate one best TP, among the equivalently photoactive four different porphyrins. The four tetraphenylporphyrins (TP) having the same absorption parameters, life time and quantum yield, having the only difference of elongated alkoxy groups.

Theory predicts that they are symmetric in nature. DFT based computation shows that HOMOTPP to LUMOC60 transition (Table 3) is most feasible on interacting.

**Table 3:** FMO energies of all four TP along with C<sub>60</sub>

Energy (eV)	1	2	3	4	C <sub>60</sub>
HOMO	-0.2648	-0.2647	-0.2646	-0.2642	-0.2400
LUMO	-0.0805	-0.0804	-0.0803	-0.0799	-0.1295



TP	-R group	$\tau_0$ (ns)	$\phi$
1	-H	8.09	0.068
2	-(CH <sub>2</sub> ) <sub>4</sub> -CH=CH <sub>2</sub>	8.07	0.123
3	-(CH <sub>2</sub> ) <sub>6</sub> -CH=CH <sub>2</sub>	8.07	0.123
4	-(CH <sub>2</sub> ) <sub>9</sub> -CH <sub>2</sub> -CH <sub>2</sub>	8.10	0.119

**Figure 2:** Tetraphenyl porphyrins (TP) used.

Mulliken charge distribution (Table 4) indicates that on complexing with 60-fullerene, e- transfer is taking place from Fullerene to TP in all cases. i.e. here fullerene will acts as donor. Chaudhuri *et al.* [6] justified this theoretical prediction experimentally.

**Table 4:** Mulliken charge distribution

TP	N (without H)	N (with H)
<b>1</b>	0.1246	-0.2008
<b>1/C<sub>60</sub></b>	0.1241	-0.2015

Now to judge discriminating ability, <sup>1</sup>H NMR spectral study is done using DFT. It indicates that in each case downward shift of pyrrolic proton is taking place on complexing. And the amount of shift (Table 5) clearly indicates complexing ability of the 4 porphyrins. This was checked by experimental determination of the binding constant of the adducts [6].

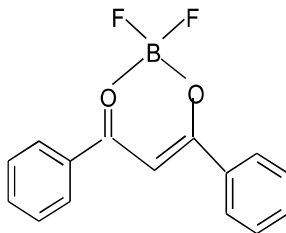
**Table 5:** <sup>1</sup>H NMR shift on complexation

Pyrrolic Proton (-NH)	δ ppm							
	1	1/C <sub>60</sub>	2	2/C <sub>60</sub>	3	3/C <sub>60</sub>	4	4/C <sub>60</sub>
	-4.184	-4.102	-4.179	-4.146	-4.172	-4.148	-4.168	-4.151
Chemical Shift (δ ppm)	0.0823 (down)		0.0331 (down)		0.0241 (down)		0.0167 (down)	

### Molecular sensing by electron deficient (Dibenzoylmethanato) boron difluoride (DBMBF2)

(Dibenzoylmethanato) boron difluoride (DBMBF2) is well known sensor of polar organic donor in ground as well as in excited state.

Indenopyridine are recently known as adenosine receptor, can be used as antagonistic activator also. We have chosen six such electron rich aromatic systems. These are non-polar hydrocarbons Naphthalene, Anthracene and Phenanthrene along with three Indenopyridines.



**Figure 3:** DBMBF2

Theory predicts that in the optimised adducts, donor and acceptor moieties are 3.5 to 4 Å apart which is very much feasible distance for charge transfer transition.

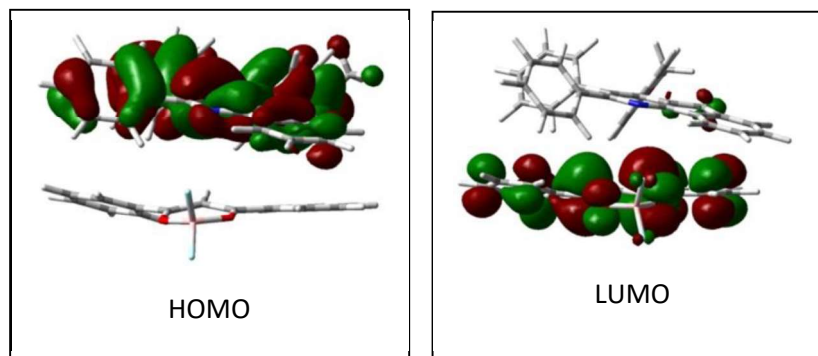
Along with charge distribution we have studied the geometry distortion pattern also on adduct formation (Figure 4). This might give the information of the extent of interaction.

The FMO feature clearly show that HOMO resides mainly on donor moiety and LUMO is on electron deficient DBMBF2.

The experimental checking of theoretical predictions are already reported by Chaudhuri et. al. [7]. It established the recognition of Anthracene and one indenopyridine by the DBMBF2 in ethanol medium through isosbestic formation [7].

System	Planner Front view	Two Ph rings (°)	Side view	Heterocycle ring/Ph-wings (°)
DBMBF2		-0.07		75.02
A2/DBMBF2		2.50		30.22
I3/DBMBF2		-8.23		-25.23

**Figure 4(a):** Angle (in degree) of distortion on adduct formation in ground state geometry optimized adduct in gas phase.



**Figure 4(b):** FMO of I<sub>2</sub>/DBMBF<sub>2</sub> adduct on ground state geometry.

## Conclusion

Thus theory can also predict the possibility of smart material designing using the small starting molecules efficiently. This type of study should be encouraged just to minimize chemical environmental hazards as well as to minimize cost. So it is a cost effective environment friendly study.

## Acknowledgements

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## References

- [1] J. Jayabharathi, V. Thanikachalam, K. Jayamoorthy, M. Venkatesh Perumal, "Spectrofluorometric studies on the binding interaction of bioactive imidazole with bovine serum albumin: A DFT based ESIPT process" *Spectrochim. Acta A* 79, 6-16, (2011).
- [2] Y. Zhao and D.G. Truhlar, "Density Functionals with Broad Applicability in Chemistry" *Acc. Chem. Res.* 41, 157-167, (2008).
- [3] K. Kim, S. J. Park, and J.-I. Choe, "DFT Conformational Study of Calix[5]arene and Calix[4]arene: Hydrogen Bond" *Bull. Korean Chem. Soc.* 29, 1893-1897, (2008).
- [4] I. Obraztsov, W. Kutner, F. D'Souza, "Metalloporphyrins in Solar Energy Conversion." *Electrochemistry of N<sub>4</sub> Macrocyclic Metal Complexes.* 171-262, (2016). Springer International Publishing.
- [5] S. Mula, A. Ray, M. Banerjee, T. Chaudhuri, K. Dasgupta, S. Chattopadhyay, "Design and Development of a New Pyrromethene Dye with Improved Photostability and Lasing Efficiency:

Theoretical Rationalization of Photophysical and Photochemical Properties” J. Org. Chem. 73, 2146-2154, (2008).

[6] T. Chaudhuri, D. Goswami, M. Banerjee, S. Chattopadhyay, S. K. Nayak. “Supramolecular selectivity of [60]-fullerene among equivalently photoactive porphyrins”, J. Lumin. 130, 1750 - 1755, (2010).

[7] T. Chaudhuri, S. Salampuria, C. Mukhopadhyay, P. K. Tapaswi, S. Chattopadhyay, M. Banerjee, “Molecular Recognition of Anthracene and Indeno-pyridine by (Dibenzoylmethanato)boron difluoride in Ethanol”, J. Photochem. Photobiol. A: Chem. 248, 55-62, (2012).