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Theoretical Investigations of photosynthetic reaction centres Using Density Functional Theory (DFT)

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Many questions of the fundamental processes in photosynthesis research remain unanswered, and several so-called artificial photosynthetic reaction centres have been developed in the course of these investigations of photosynthesis. Our approach to design most efficient porphyrins for the charge transfer is based on tetraphenyl porphyrins (TPP) substituted with electron donating groups and electron acceptor groups, which are not on the porphyrin moiety but are separated by a spacer, which will enhance the electronic communication between the donor and the acceptor. The high charge transfer will lead to a high value for the first static hyperpolarizability (β), a measure of NLO activity.

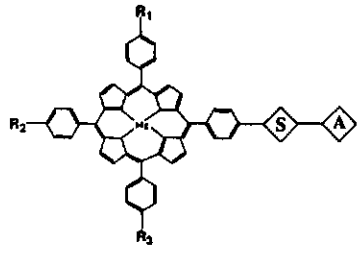
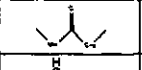
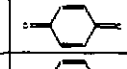
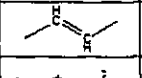
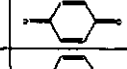
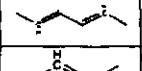
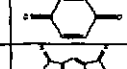
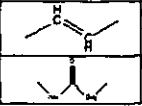
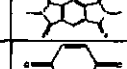
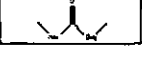


Figure 1.0. Structure of Artificial photosynthetic reaction centre

A comparative investigation of the first static hyperpolarizabilities (β) of TPP derivatives with a number of Spacer(S)-Acceptor(A) moieties on either side of the TPP ring system enhancing the π-electronic charge distribution through the π-conjugation is reported in this research. The first static hyperpolarizabilities (β) of TPP derivatives were obtained by Density Functional Theory (DFT). Referring to the data in table, increasing of β can be seen along the porphyrins 2 to 4, due to the effectiveness of the charge transfer along the spacer molecules. In both porphyrins 3 and 5 have the same spacer but different acceptors. The high value of β in porphyrin 5 is due the substitution of pyromellitimide instead of quinine as an acceptor. According to the investigation, it can be concluded that the spacer and the acceptor molecules play a major role in the intra-molecular charge transfer between the donor and the acceptor leading to a very large value for β. Hence, these molecules behaved potential artificial photosynthetic reaction centres with high charge transfer ability. Thus, these molecules can also be used as NLO materials for photonic devices.

Table 1.0. Calculated hyperpolarizability (β_{tot}) values for all the molecules

1	H	-	-	# b3lyp/3-21g	1.540
				# b3lyp/6-31g	1.345
2	H			# b3lyp/3-21g	5.188
				# b3lyp/6-31g	13.149
3	NH_2			# b3lyp/3-21g	130.836
				# b3lyp/6-31g	279.760
4	NH_2			# b3lyp/3-21g	684.922
				# b3lyp/6-31g	737.051
5	H			# b3lyp/3-21g	134.350
				# b3lyp/6-31g	171.337
6	R_1,R_3=H R_2=Carotenoid			# b3lyp/sto-3g	434.008

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