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In Silico Design to Explore the Effect of Metalloporphyrin and C_{60} Cage on the non-linear optical (NLO) Properties

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Abstract

The uses of nonlinear optical (NLO) materials in photonics, optoelectronics, optical switching, and data storage have drawn a lot of interest. This work provides a theoretical analysis of how Zn-porphyrin and fullerene (C_{60}) cage affect the NLO characteristics of four designed systems: MP1, MP2, MP1C_{60}, and MP2C_{60}. To optimize molecular geometries and assess important parameters like HOMO-LUMO energy gaps, dipole polarizability, and first order hyperpolarizability, Density Functional Theory (DFT) calculations using the B3LYP functional were utilized. MP2 showed improved charge delocalization with the smallest energy gap (0.376 eV). Fullerene's function as an efficient electron acceptor was confirmed by functionalization with C_{60}, which changed the electronic distributions in MP1C_{60} and MP2C_{60}. Structural stability was demonstrated by the Zn-N bond lengths remaining constant at 2.07 nm. Significant improvements were seen in polarizability and hyperpolarizability, especially for MP2C_{60} (β_{total} = 78128.92×10^{-30} esu). According to these results, metalloporphyrin and C_{60} work in concert to significantly enhance NLO

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performance, making these hybrids attractive options for cutting-edge photonic and optoelectronic applications.

Keywords: NLO; Metalloporphyrin; C_{60} cage; DFT; HOMO-LUMO energy level; Polarizability; First order polarizability

1. Introduction

In recent decades, the scientific discipline of non-linear optics has experienced remarkable growth. It is predicated on the phenomenon of powerful coherent light radiation interacting with matter. The study of how light interacts with matter in situations where the atoms' non-linear response is significant is known as non-linear optics [1]. Organic compounds with NLO properties became unmatched in popularity and dominance in a variety of fields, including medicine, material science, atomic, molecular, and solid-state physics, surface interface sciences, and chemical dynamics, as a result of the quick development of high-tech electronic, optical, and storage devices [2,3]. Many materials, including graphene [4,5], fullerene [6], and quantum dots [7,8], have garnered scientific interest in recent decades due to their noteworthy nonlinear optical (NLO) characteristics. The study of organic and organometallic chromophores has also received a great deal of attention. In these cases, nonlinearity is primarily caused by the so-called push-pull architecture, which consists of a donor and an acceptor moiety connected by a π-delocalized spacer [9]. The NLO characteristics of the fundamental molecules dictate the NLO characteristics of the materials. Modeling organic molecules with high NLO characteristics is beneficial when using this criterion [10,11]. Appropriate donor-π-spacer-acceptor (D-π-A) systems with structurally modifiable features are required to model and build high-response NLO materials. In this way, substitution is a key component in the conjugation modification and, consequently, the NLO activity [12,13]. A lot of work has gone into getting very effective NLO materials. It is commonly recognized that altering the donor and acceptor capacities and prolonging the π-conjugated bridge can control the molecular second-order NLO characteristics. The electronic intramolecular charge transfer (ICT) of the molecule is linked to the initial hyperpolarizability and, consequently, the second-order NLO response [14,15].

Because of their structural diversity and ease of chemical alteration, porphyrins and metalloporphyrins are frequently employed as field-responsive materials in optoelectronics. Their ligands are useful for nonlinear optical applications because they offer significant dipole moments, polarizabilities, and hyperpolarizabilities. The potential of polymeric porphyrins in innovative

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materials applications is increased by their remarkable low-dimensional conductivity [16]. Porphyrins have garnered a lot of interest as an organic material with an elevated nonlinear optical susceptibility in the hunt for better third-order nonlinearity materials because of their large p-electron system with 2D conjugated molecular arrangements as well as the presence of 1D delocalized electrons [17]. Because of their high solubility, probable processability as layers, and thermal and chemical durability, 2D structures based on delocalized macrocycles, including porphyrins and metal porphyrins, have garnered a lot of interest [18]. Furthermore, they can easily create an electronic exchange in a push-pull system by using their polarizable conjugated ring as a linker, which is necessary for a significant second order NLO response [19]. To create different donor-(π-conjugated bridge)-acceptor (D-π-A) and D-π-D systems, porphyrins and metalloporphyrins can be utilized as π-conjugated bridges [20,21]. Previous research showed that metal complexation and the type of suitable donor-acceptor substituents can readily adjust the NLO characteristics of porphyrins [22-24].

A network of fused carbon atoms forms the spherical carbon cage known as fullerene molecules. Specifically, C_{60} fullerene is made up of 60 carbon atoms organized in a highly symmetrical configuration [25]. Since buckminsterfullerene (C_{60}) characterization, fullerenes and its derivatives have garnered a lot of attention due to their special physicochemical characteristics, which are helpful in a variety of material science applications [26-28]. The polyhedral counterparts of two-dimensional graphene sheets are called fullerenes. Though in trace proportions, they have been found in interplanetary space and are found in nature [29-31]. Because of its distinct physical and molecular characteristics, C_{60} has garnered a lot of scientific attention [32]. The most significant features of C_{60} are by far its extremely symmetric structure, its capacity for multiple addition processes, and its remarkable electron-accepting capabilities (e.g., it can take on up to six electrons) [33]. A number of the applications are still in their infancy, and fullerenes have only lately been employed in innovative optical applications, cancer therapy, and noninvasive cancer imaging. Future studies will examine the fullerene C_{60}'s uses in catalysis, water purification, biohazard prevention, portable electricity, automobiles, and medicine [34].

Nanostructured thin films with tunable sizes enable charge carrier confinement, making them essential for optoelectronic applications [35]. Various advanced materials, including rare-earth-doped up-converting systems, polyoxometalates, metal nanoclusters, and cage-cluster frameworks, have been explored for nonlinear optical (NLO) applications due to their unique

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optical and electronic properties, although some are limited by low efficiency or slow development [36-39]. In particular, Ag/Au nanoclusters and silver alkynyl systems exhibit strong quantum confinement and ultrafast response, making them promising for optoelectronics and all-optical switching [38,40]. Additionally, switchable NLO materials based on redox and photoresponsive mechanisms have gained attention for electro-optic applications [41]. Experimental studies, such as femtosecond Z-scan on TiO_2 nanoparticles, further confirm strong NLO responses, highlighting the broad potential of these materials in advanced photonic technologies [42].

We are now working to ascertain the hybrid composites' NLO responses to metalloporphyrin-C_{60} cages. To put it briefly, we have theoretically created four hybrid composites using Zn-porphyrins and C_{60} fullerenes in our research. We employed DFT calculations to forecast these composites' NLO response. In order to investigate the suggested molecules' NLO response, a number of metrics have been calculated, including linear polarizability, second-order nonlinearity, HOMO-LUMO gap, and charge transfer mechanism. For upcoming photonic and electronic devices, these hybrid materials might provide strong and adjustable NLO responses. The intelligent development of future optical materials can be guided by this method.

2. Computational Insights

The Gaussian 09 computational software is used to carry out the density functional theory (DFT) calculations [43]. Of the several DFT techniques that are available, we have chosen the B3LYP method [44], which combines the Lee, Yang, and Parr correlation functional (LYP) with Becke's three-parameter hybrid exchange functional (B3) [45]. In addition, B3LYP is accessible in the majority of quantum chemistry software packages and is quite simple to use [46]. Because of its accuracy in forecasting molecule structures and other properties, B3LYP is used in computational chemistry simulations in conjunction with the 6-311G basis set. Geometry optimization was performed using DFT theory at the B3LYP/6-31G* level [47].

Finding the smallest point of energy is the aim of geometric optimization calculations since it represents the actual molecule structure and is used to compute bond length, bond angle, and other characteristics. The 6-311*G was found to be appropriate for the atoms of H, O, and N [48]. While LANL2DZ (Los Alamos National Laboratory 2-double-z) associated with pseudo-potential was used for zinc (Zn). Selecting an appropriate model and calculation technique is essential for quantum chemical research in order to gather precise data and comprehend the connection between the computed outcomes and physical characteristics. The B3LYP approach is appropriate for

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fullerene systems since several groups have used it and had satisfactory findings, and density functional theory is being utilized extensively in calculations because of its rather acceptable accuracy and affordable cost [49-51]. Additionally, the NLO properties of the optimized molecules had been taken into account. Using the same level of basis set and functional utilized for optimization, the first hyperpolarizabilities for each chemical system were found to determine the NLO characteristics. To further comprehend the charge transfer process in the investigated push-pull compounds, HOMO-LUMO analysis was also carried out.

First order polarizability and first-order hyperpolarizability were examined using an additional computational approach. The following formulas are used to determine hyperpolarizability $<\beta>$ and polarizability $<\alpha>$. First order polarizability is computed using equation (1) [52].

$$<a> = 1/3(a_{xx} + a_{yy} + a_{zz}). \quad (1)$$

Whereas for the calculation of first order hyperpolarizability, we use the equation (2) [53].

$$<\beta> = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

Where

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2} \quad (2)$$

For a deeper understanding of the process of nonlinear polarization, we first consider first order polarizability (α), which represents an estimate of the degree of linear polarization under the influence of an electrical field. We have calculated the values of the first order polarizability (α) components for each compound using the mathematical equation (1). The magnitude of first order hyperpolarizability is calculated using equation (2).

3. Geometric Structure

Based on the Zn-porphyrin (Zn-P) and carbon 60 cage shown in Figure 1, we have created four push-pull molecules (MP1, MP2, MP1C_{60}, and MP2C_{60}) using DFT insights. The optimized bond distances are provided in Table 1. The zinc porphyrin core that serves as the main light-harvesting donor is the foundation of these four systems. The efficiency of charge transfer from the donor to the fullerene acceptor can be predicted by methodically altering the linkers and peripheral groups [54].

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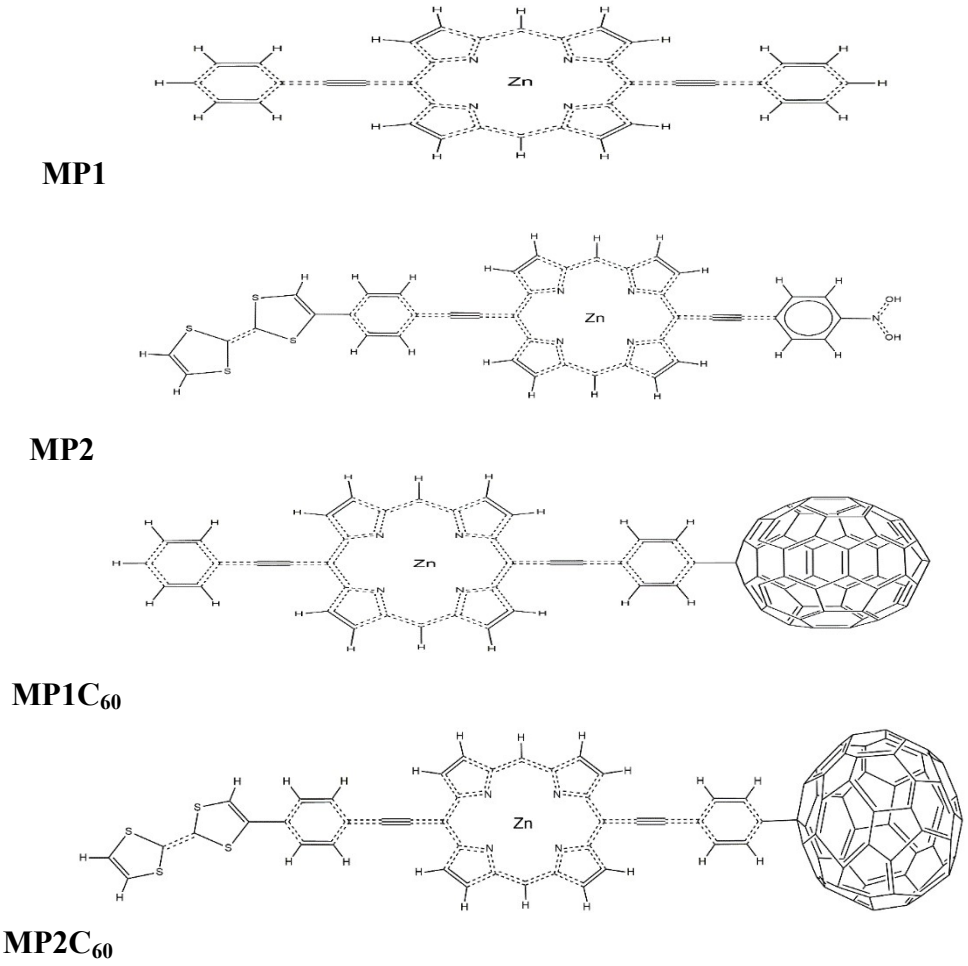

Figure 1. Chemical structures of the investigated systems: MP1, MP2, $MP1C_{60}$ and $MP2C_{60}$.

Table 1: Computed bond lengths in nm for all the four designed compounds

Geometrical parameters	MPPP1	MPPP2	$MPPP1C_{60}$	$MPPP2C_{60}$
Zn-N	2.07 (2.0) *	2.07	2.07	2.07

We selected Zinc (Zn) porphyrin and Fullerene (C_{60}) for their efficient donor-bridge-acceptor (D-π-A) system, where a conjugated π-spacer facilitates rapid intramolecular charge transfer (ICT). This architecture promotes extensive electron redistribution under light, yielding high polarizability and enhanced second- and third-order hyperpolarizabilities, making the composite suitable for optical limiting, frequency modulation, and high-speed switching.

In MP1, there is a charge shift from Zn-porphyrin to the aromatic rings, indicating that the aromatic rings are acting as an electron attractor or acceptor and the Zn-porphyrin cage as an electron donor. TTF-based donor substituents that are affixed to the porphyrin framework in MP2

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improve intramolecular charge transfer and electron-donating capacity. The aromatic rings serve as an electron donor for $MP1C_{60}$ and $MP2C_{60}$, while the fullerene cage acts as an electron acceptor. Adding another fullerene to the opposite side of $MP2C_{60}$ would create a symmetric acceptor system, which could reduce directional intramolecular charge transfer (ICT) and partially lower nonlinear optical (NLO) efficiency. However, depending on conjugation and orbital alignment, it might enhance light absorption or stabilize excited states, so the overall NLO response would depend on molecular symmetry, orbital distribution, and electronic coupling.

When compared to porphyrin alone, the nonlinear optical (NLO) capabilities are greatly enhanced by the presence of fullerene. Although $MP1C_{60}$ is a small and effective model for quick electron transport, $MP2C_{60}$ functions as a more potent "molecular wire" thanks to its longer bridge. This $MP2C_{60}$ is intended to optimize the nonlinear optical response, thereby creating a more potent contender for laser protection and high-performance photonic devices.

4. Results and Discussion

To investigate the NLO response of the suggested molecules, a few metrics were calculated, including linear polarizability, second order nonlinearity, HOMO-LUMO gap, and charge transfer mechanism. To characterize the chemical reactivity of the hybrid compounds, we have first described the HOMO-LUMO energy differential displayed in Fig. 2. All the compounds have smaller energy gaps, which suggests that there is a substantial charge transfer between the molecules. The easier the charge transfer, the smaller the energy gap between the HOMO and LUMO. Table 2 below shows the HOMO-LUMO energy differential.

TABLE 2: Computed HOMO-LUMO energy difference (eV) for the designed molecules

COMPOUND	MP1	MP2	$MP1C_{60}$	$MP2C_{60}$
E_{HOMO} (eV)	-10.877	-9.369	-9.162	-8.220
E_{LUMO} (eV)	-9.796	-8.933	-8.244	-7.507
$\Delta E = E_{LUMO} - E_{HOMO}$ (eV)	1.081	0.436	0.918	0.714

The designed molecules have HOMO energies between -10.877 and -8.220 eV and LUMO values between -9.796 and -7.507 eV. One crucial indicator of intramolecular charge transfer effectiveness and molecular electronic softness is the shrinking HOMO-LUMO energy gap. The magnitude of the electronic transmission between these units determines the bandgap. The non-

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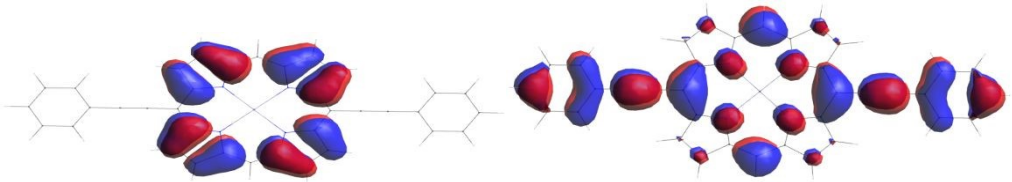
linear variation in gap values can be caused by various linkers, such as ethynylenephenylene, which can either help or hinder this coupling. MP1 has the largest energy gap (1.081 eV) of any system under study, which suggests comparatively poorer electronic polarizability and charge transfer capacity. MP2, on the other hand, exhibits the lowest bandgap (0.436 eV), indicating better electronic delocalization and increased charge transport inside the molecular structure. MP2 has tetrathiafulvalene (TTF) derivatives (the sulfur-containing rings on the left), which contribute to the lower bandgap. Due to their minimal energy gap and intramolecular charge transfer (ICT), TTF derivatives are incredibly potent electron donors [55]. A extremely delocalized "electronic highway" can go throughout the entire molecule thanks to the structure of MP2. The "ground state" (HOMO) and "excited state" (LUMO) have very little energy difference when electrons are allowed to flow around a flat, conjugated system.

The complexes $MP1C_{60}$ and $MP2C_{60}$, which include fullerene, have intermediary bandgap values that are 0.918 eV and 0.714 eV, respectively. As demonstrated in porphyrin-fullerene hybrid materials, where LUMO and HOMO are specifically localized on acceptor/donor parts of the molecule, the presence of an electron acceptor, such as fullerene, in D-A systems tunes frontier orbital energies and leads to charge transfer properties that affect nonlinear optical response [33]. Because of the steric barrier caused by the bulky fullerene's attachment, these complexes have a greater bandgap than MP2. By altering the orbitals' planar alignment and decreasing the effective conjugation, this crowding can distort the molecule structure and raise the HOMO-LUMO gap. Because $MP2C_{60}$ keeps the TTF-like donor groups from MP2, that are far more potent donors than the straightforward phenyl/alkyne groups in $MP1C_{60}$, its bandgap is lower than $MP1C_{60}$. Overall, the decreasing bandgap trend follows the order:

$MP1 > MP1C_{60} > MP2C_{60} > MP2$

Figure 2 displays the chemical orbitals involved in these four molecules' main electron transitions.



HOMO LUMO

MP1

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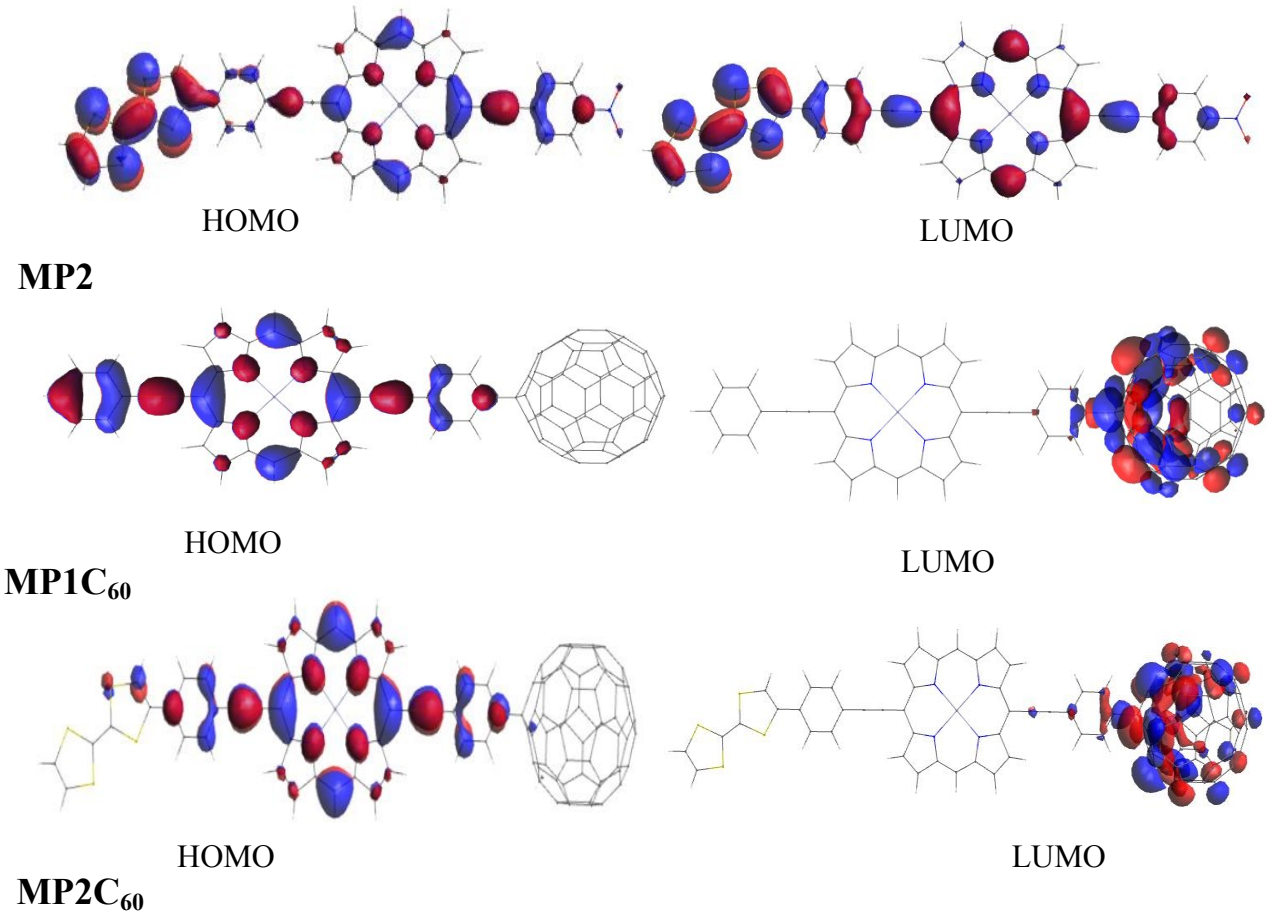

Figure 2. The frontier molecular orbitals of four designed molecules involved in the dominant electron transitions.

Examining the physical mechanism pertaining to the determination of the first order polarizability (a) is equally crucial for the consideration of the first order hyperpolarizability (β). First order polarizability is calculated using Equation 1. Table 2 shows the calculated dipole polarizability coefficients for four compounds.

Table 3: First order polarizability elements (in 1×10^{-30} esu) for the four designed compounds

Comp	a_{xxx}	a_{yyy}	a_{zzz}	$<a>$
MP1	4.57	20.58	1.08	8.74
MP2	52.12	5.98	1.62	19.91
$MP1C_{60}$	28.59	8.49	5.07	14.05

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$MP2C_{60}$	136.55	9.83	5.81	50.73

The first order polarizability tensors a_{ii} (i = x, y, z) for four chosen molecules are nonzero. According to the polarizability tensor study, MP2, $MP1C_{60}$, and $MP2C_{60}$ show the highest polarizability along the x-axis, suggesting that the molecular backbone is where the majority of electron delocalization and charge transfer takes place. Conversely, MP1 exhibits more polarizability along the y-axis, indicating a distinct electron density distribution and much less longitudinal conjugation. Fullerene's attachment improves directional charge transfer along the x-axis because of its strong donor-acceptor interaction and extended π-conjugation.

The HOMO-LUMO bandgap and polarizability are typically inversely correlated in molecular systems [56]. Ahsin *et al.* (2024) establish that polaron formation in conducting polymers induces a significant reduction in the HOMO-LUMO energy bandgap (ΔE), resulting in a dramatic increase in the first hyperpolarizability (β). This robust inverse relationship, where decreased excitation energy leads to enhanced nonlinear optical (NLO) response, shows β values increasing by up to 246 times in polaronic states [57]. An external electric field can more readily deform electrons with a smaller energy gap because they are less firmly attached to the nuclei. For example, MP2's average polarizability is 19.91 compared to 8.74, a direct result of its substantially shorter bandgap (0.436) than MP1's (1.081). Polarizability rises with molecular size and the degree of π-conjugation, according to structural analysis. By adding the big, electron-dense C_{60} fullerene cage to the porphyrin structures, a vast reservoir of non-alignable electrons is created, which increases the first order polarizability values by "stretching" the electron cloud.

Electrons can move along the whole length of the TTF derivative, porphyrin, and fullerene units in long, linear molecules like the $MP2C_{60}$ triad. Adding groups like fullerenes can occasionally raise the bandgap by stabilizing the molecule's ground state, but first order polarizability is higher than that of all other compounds. Historically, the molecules have been divided into two categories: orbital controlled (soft-type) and charge controlled (hard-type). The soft-type relies on a molecule's capacity to transfer charge either instantly or permanently, whereas the hard-type relies on the molecule's uneven charge distribution. Due to their increased sensitivity to external perturbations, the border molecular orbitals are particularly implicated in soft-type interactions [58]. Despite having more electrons and being a bigger molecule, $MP1C_{60}$'s bandgap (0.918 eV) is above double that of MP2 (0.436 eV). The increased excitation energy needed for

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$MP1C_{60}$ produces a relatively stiff electron cloud that is less sensitive to an external electric field since polarizability and bandgap are negatively correlated. On the other hand, MP2's electron cloud is more flexible and easily polarizable due to its narrower bandgap, which makes electrical excitation simpler. As a result, $MP1C_{60}$ has a rather hard molecular nature with little electron cloud deformability, while MP2 has a softer molecular nature with better intramolecular charge transfer and increased polarizability. First order polarizability of four designed molecules decreases in following order.

$MP2C_{60}$ > MP2 > $MP1C_{60}$ > MP1

Table 4 shows the total hyperpolarizability (β_{tot}) and the calculated first-order hyperpolarizability tensor components (β_{xxx}, β_{xxy}, β_{xyy}, etc.) for MP1, MP2, $MP1C_{60}$, and $MP2C_{60}$ by using equation 2.

Table 4: Computed values of first order hyperpolarizability tensors (1×10^{-30} esu) for all the compounds

Tensors	MP1	MP2	$MP1C_{60}$	$MP2C_{60}$
β_{xxx}	0.00003917	-1418.692	-5702.829	78021.079
β_{xxy}	0.00070914	104.031	-10.591	-2395.119
β_{xyy}	-0.003496	28.205	-8.881	20.642
β_{yyy}	0.003226	2.266	0.538	10.432
β_{xxz}	0	-14.797	107.097	2315.702
β_{yyz}	0	- 0.353	-1.787	-2.881
β_{xzz}	-0.00000339	-0.918	0.10038	16.416

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β_{yzz}	0.000000332	0.0257	-0.752	-1.765
β_{zzz}	0	0.013	5.006	2.391
β_{tot}	0.00524	1395.54	5712.68	78128.92

Following order MP1 << MP2 < $MP1C_{60}$ << $MP2C_{60}$, the calculated first-order hyperpolarizability (β_{tot}) exhibits a noticeable increase across the systems under study. Because polarizability and first order hyperpolarizability reflect essentially different ways that molecules react to an electric field, their values do not follow the same upward trend. As molecules get longer from MP1 to $MP2C_{60}$, polarizability (a), a linear property, increases proportionately with the molecular volume and total amount of electrons.

The first order hyperpolarizability, on the other hand, is a nonlinear feature that only depends on the extent of intramolecular charge transfer (ICT) and structural asymmetry. First order hyperpolarizability needs a "push-pull" system in which an electron-donating group is joined to an electron-accepting group by a conjugated bridge, whereas polarizability only needs room for electrons to move. Compared to systems incorporating fullerene, MP1 and MP2 exhibit reduced hyperpolarizability due to their stiffer electron clouds, absence of prolonged π-conjugation, and limited intramolecular charge transfer. The enhanced hyperpolarizability (β) of MP2 relative to MP1, prior to fullerene attachment, arises from the presence of stronger electron-donating TTF derivative, which increase intramolecular charge transfer and extend π-conjugation within the molecular framework. The sulfur-containing rings improve electron delocalization and polarizability due to their higher electron density and polarizable nature, leading to greater charge separation under an applied electric field. In contrast, the phenyl groups in MP1 exhibit comparatively weaker electron-donating ability and limited conjugation efficiency. As a result, MP2 demonstrates a more pronounced nonlinear optical response than MP1 even before the incorporation of Fullerene C_{60}, highlighting the intrinsic contribution of its molecular architecture to the observed increase in β.

C_{60} is a common compound used in multicomponent molecular architecture to adjust its optical properties to certain spectral regions of interest because of its high electron-accepting capabilities and exceptionally small reorganization energy (ca. 0.23 eV). By employing chemical techniques, the average hyperpolarizabilities in fullerene derivatives are greatly enhanced by the C_{60} moiety,

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which functions as an electron acceptor in the ground electronic state [6]. The delocalization of charge from the electron-rich moiety to the electron-poor carbon cage, which results in partially negatively charged fullerene moieties, is primarily responsible for the observed increase. Chemical changes including a range of organic moieties that donate electrons have therefore been investigated [59]. Extended π-conjugation and a robust donor-acceptor (D-A) design cause the linear polarizability (α) and second-order hyperpolarizability (β) to grow from MP1 to $MP2C_{60}$. Due of its symmetric electronic distribution and large HOMO-LUMO gap (ΔE), which restricts excitation, MP1 exhibits the lowest NLO response. $MP2C_{60}$, on the other hand, has a powerful push-pull mechanism that allows for intense intramolecular charge transfer (ICT) by using the TTF derivative as a strong donor and C_{60} as a strong acceptor. A LUMO on the C_{60} cage and a HOMO on the donor section are shown by FMO analysis. The two-state model states that $MP2C_{60}$'s reduced bandgap improves the transition dipole and dipole change upon excitation, leading to better NLO performance.

By introducing a powerful electron-accepting unit, the fullerene attachment in $MP1C_{60}$ creates a donor-acceptor system that facilitates intramolecular charge transfer (ICT) from the donor backbone to the fullerene acceptor. The dominating β_{xxx} tensor component reflects the fullerene's ability to increase the π-conjugation length, which facilitates electron delocalization along the molecular axis. By lowering the excitation energy across the charge-transfer pathway, this prolonged conjugation and improved ICT cause β_{tot} to increase fourfold in comparison to MP2. The smaller π-conjugation pathway and poorer donor-acceptor strength of $MP1C_{60}$'s molecular framework are the main causes of its lower initial hyperpolarizability when compared to $MP2C_{60}$. $MP2C_{60}$ has a longer, electron-rich donor system that is connected to the C_{60} electron-acceptor moiety which enables a much larger and more effective Intramolecular Charge Transfer (ICT). The first hyperpolarizability is a nonlinear property that increases exponentially with the distance from which electrons can be displaced. $MP1C_{60}$'s shorter bridge and smaller donor moiety restrict the amount of electronic polarization, although having the same potent fullerene acceptor. As a result, $MP2C_{60}$ has a big β_{xxx} tensor component and a total β value that is more than thirteen times greater than that of $MP1C_{60}$. This indicates both more structural asymmetry and greater electronic polarization due to enhanced intramolecular charge transfer. Overall, the remarkable improvement in hyperpolarizability for $MP1C_{60}$ and $MP2C_{60}$ is mostly caused by the addition of fullerene to these molecules, as well as ideal donor-acceptor geometries and prolonged conjugation. Of the

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systems under study, $MP2C_{60}$ has the highest polarizability and hyperpolarizability, making it the most promising option for nonlinear optical applications as shown in Table 5.

Table 5: HOMO-LUMO energies, bandgap, polarizability (α), and hyperpolarizability ($\beta\times10^{-30}$ esu) of MP1, MP2, $MP1C_{60}$, and $MP2C_{60}$.

Comp	MP1	MP2	$MP1C_{60}$	$MP2C_{60}$
HOMO (eV)	-10.877	-9.369	-9.162	-8.220
LUMO (eV)	-9.796	-8.933	-8.244	-7.507
Bandgap (eV)	1.081	0.436	0.918	0.714
Polarizability (α) (1×10^{-30} esu)	8.74	19.91	14.05	50.73
Hyperpolarizability (β) (1×10^{-30} esu)	0.00524	1395.54	5712.68	78128.92

The reported NLO coefficients are theoretically calculated using DFT/TD-DFT methods, and no experimental measurements have been performed; experimental verification is suggested as future work. However the suggested Zn porphyrin-bridge-fullerene molecules can be produced by attaching stiff ethynyl spacers and thiophene units to the porphyrin core by well-known palladium-catalyzed cross-coupling processes, such as Sonogashira or Suzuki reactions. The carbon cage can then be precisely functionalized by covalently joining the fullerene (C_{60}) moiety by high-yield "click-like" reactions like the Bingel reaction or the Prato reaction. The conjugation length and donor-acceptor distance, which are critical for adjusting the nonlinear optical (NLO) characteristics and guaranteeing the stability of the finished composite, can be precisely controlled using these modular synthetic approaches.

In a related study, the first-order hyperpolarizability (β) of para-aminobenzoic acid is 29.99×10^{-30} esu, indicating moderate nonlinear optical (NLO) behavior [60]. In contrast, the $MP2C_{60}$ system exhibits a significantly higher β of 78128.92×10^{-30} esu an enhancement of approximately 2600-fold due to strong intramolecular charge transfer, extended π-conjugation, and a smaller band gap (0.714 eV). Urea-barbituric acid (UBA) crystals that have been investigated experimentally exhibit significant third-order NLO activity and effective optical limiting, but their high band gap (~4.50 eV) restricts charge transfer, decreasing first-order hyperpolarizability [61]. Excellent third-order NLO capabilities are also displayed by morphology-dependent MoS_2 nanoplatelets, which have a low optical limiting threshold (0.73×10^{12} W/m^2) and a high nonlinear absorption

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coefficient (5.9×10^{-10} m/W) [62]. Overall, UBA and MoS_2 are very successful in third-order nonlinear absorption-based optical limiting, highlighting distinct NLO regimes, but $MP2C_{60}$ is superior in second-order NLO response.

Conclusion

Bandgaps, polarizabilities, and first order hyperpolarizabilities of MP1, MP2, $MP1C_{60}$, and $MP2C_{60}$ were used to study their NLO characteristics. Because of its stiff electron cloud and little intramolecular charge transfer, MP1 exhibits the highest bandgap and minimum polarizability, leading to negligible hyperpolarizability. MP2, which has a moderate polarizability and a narrower bandgap, shows a notable rise in β because of higher electron delocalization and donor-acceptor alignment. NLO responsiveness is significantly improved by fullerene connection in $MP1C_{60}$ and $MP2C_{60}$. Extended π-conjugation and fullerene-induced charge transfer cause $MP1C_{60}$ to exhibit higher β, whereas excellent donor-acceptor geometry, extended conjugation, and greatly delocalized electrons cause $MP2C_{60}$ to exhibit the highest β. These findings demonstrate that while bandgap affects NLO behavior, the main determinants of first order hyperpolarizability are charge-transfer efficiency, conjugation duration, and molecule structure, which makes $MP2C_{60}$ an extremely interesting option for nonlinear optical uses.

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The data that support the findings of this study are available from the corresponding author via email.

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