Bithieno Thiophene-Based Small Molecules for Application as Donor Materials for Organic Solar Cells and Hole Transport Materials for Perovskite Solar Cells

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1. INTRODUCTION

The skyrocketing energy consumption appears to be a major stumbling block in satisfying the requirements of a dynamically developing world population. Although fossil fuels provide 80 percent of the world’s energy needs, burning of carbonaceous stores produces tons of CO₂, which contributes to global warming. Scientists are progressively keen on finding amiable and sustainable wellsprings of energy that have a continuous and sustainable impact on the economy as energy utilization increases.¹ The photovoltaic effect (first discovered in 1839 by Edmund Becquerel) is one of the best tools for converting the sun’s inexhaustible energy into electricity.² Different technologies are based on this principle, organic photovoltaics (OPVs) being the dominant one, thanks to their minimal expense potential, semitransparency, and adaptability.³ They made use of light-capturing organic materials that could be synthesized.⁴−⁶ Until recently, inorganic silicon-containing solar gadgets were considered to be the most useful and productive constituents for solar cell assembly. Because of their rigid design, low proficiency, and high cost, their applications have been severely limited.⁷

As a solution to energy crisis, OPVs have attracted a great deal of attention. OPV systems are thought to be more compelling due to their flexible and tunable energy levels. In addition, OPVs’ surface morphology makes them more absorbent, and their high purity makes them more productive than inorganic alternatives.⁵,⁶ The working efficiency of...
fullerene organic solar cells (OSCs) has grown by 11.7% over the past few decades. However, due to poor absorption in the visible region, small band gaps, and expensive sanitization and assembly, the non-fullerene (NF) alternative options got the lead in the last few decades. The high synthetic flexibility, full spectral coverage, ease of structural adaptability, tunable optoelectronic properties, and low voltage losses of NFAs satisfied the shortages as well as empowered to accomplish the power conversion efficiencies (PCEs) of over 17 percent.

Furthermore, the general problem regarding OSCs is efficiency that is much lower than that of inorganic-based devices, which is a major flaw at the moment. The reason for this is that organic semiconductors have a substantially larger band gap than inorganic semiconductors. That is why researchers and industry have recently become engaged in perovskite solar cells (PSCs) composed of metal halide because of their interesting photophysical properties, high operational efficiency, and considerable potential in terms of low-cost assembling techniques. The tremendous instability of high yielding perovskite devices toward air, water, moisture, light, and heat might be owing to instability in both the perovskite and transporting layers. The lack of stability caused by frequently employed hole transport materials (HTMs) with dopants is one hurdle for marketing of PSCs. These hygroscopic dopants not only degrade long-term stability by allowing moisture and ion diffusion but also add to the complexity and total expense. As a result, the development of dopant-free HTMs is extremely important. As a result, the focus of this research is on selecting appropriate organic materials for use as HTMs in solar cell technology. Dopant-free bithieno thiophene (BTTI) central core-based HTMs are highly anticipated for their potential to provide PSCs with good consistency and long-term durability. Due to the more expanded and conjugated system, MPA-BTTI adopted an H-aggregation style, resulting in more efficient charge transportation and better hole mobility. With a root-mean-square (rms) roughness of 0.44 nm, the MPA-BTTI film had a considerably smoother surface. Due to the low hysteresis, improved thermal stability, and long-term stability, the MPA-BTTI-based dopant-free PSCs achieve a phenomenal efficiency of 21.17 percent. The MPA-BTTI’s film morphology and well-aligned energy levels are credited with this accomplishment. MPA-BTTI showed tremendous energy-level synchronization with the perovskite layer, suitable hole transport, and brilliant film shape.

Twelve small donor molecules (MPAM1–MPAM12) have been drafted by thiophene-bridged end-capped acceptor engineering of already synthesized MPA-BTTI taken as reference (MPAR) in the current study. The methoxy group of MPAR has been substituted with different acceptor moieties in all designed molecules. Herein, cyano-, fluoro-, and carbonyl-containing thiophene-bridged acceptor moieties have been substituted in the MPAR-conjugated framework to tune its optoelectronic properties. Cyano, fluoro, and carbonyl groups have potential to congest the band gap, escalate the molecular conjugation, and push the absorption toward a longer wavelength by attaching to the conjugated framework of the molecule. All reported molecules constitute 4-methoxy-N-(4-methoxyphenyl)-N-phenylalanine as the donor and imide-based thiophene derivative as the acceptor moiety. The phenylamine empowers productive hole transport, while the imide-functionalized centers guarantee great intermolecular $\pi-\pi$ stacking because of their planar molecular layout. The foundation of the acceptor moiety is 2,2′-bithieno[3,2-b:3,2-c]thiophene to tune subatomic arrangements along with resultant optoelectronic and film morphological properties. In MPAM1–MPAM6, thiophene-bridged end-capped acceptor engineering has been performed on both side terminals of MPAR, while in MPAM7–MPAM12, the structural alteration has been performed on one side terminals only, as shown in Figure 1. This paper describes many design concepts for high-performance small donor molecules for proficient OSCs and productive HTMs for PSCs, which display similar optoelectronic properties, but different molecular configuration and film properties, in a synergistic manner. A new route for building high-performance dopant-free HTMs in PSCs has been opened by the results, which confirm the usefulness of designed strategies.

2. RESULTS AND DISCUSSION

In this current report, first, the absorption profile of the model molecule (MPAR) was computed via the five DFT functionals (B3LYP, CAM-B3LYP, MPW1PW91, PBEOPBE, and WB97XD) in the gaseous phase (Figure 2a) and DCM solvent, as displayed in Figure 2b. The $\lambda_{\text{max}}^\text{exp}$ of the reference molecule (MPAR) achieved by MPW1PW91 (596 nm) under 6-311G (dp) show precise compromise with $\lambda_{\text{max}}^\text{exp}$ (532 nm), as displayed in Figure 3. Therefore, all computational simulations of all freshly designed molecules have been carried out via MPW1PW91/6-311G (dp).

2.1. Structural Optimization, Dihedral Angle ($\theta$), and Bond Length ($d$). Molecular geometry has a notable impact on optoelectronic properties. The optimally selected DFT functional has been used to optimize the model molecule (MPAR) together with the currently designed molecules (MPAM1–MPAM12).Figure S1 (in the Supporting Information) shows the optimized framework of all reported chromophores. The optimized geometry is manifesting that the central acceptor core has arrayed itself in one plane, while the thiophene bridge alongside acceptor units have lined up themselves out of the plane to limit the potential energy surface.

Examined dihedral angles ($\theta$) and bond lengths ($d$) of chromophores are illustrated in Scheme 1.

Herein, $\theta_1$ and $d_1$ are the dihedral angle and bond length between the TPA moiety and thiophene bridge, respectively, whereas $\theta_2$ and $d_2$ are the dihedral angle and bond length between the thiophene spacer and acceptor group, respectively. It is evident from Table 1 that values of bond length $d_1$ and $d_2$ lie in the range of 1.36–1.46 and 1.41–1.43 Å, respectively, commending the presence of double and triple bonds leading to aggrandized conjugation. The reduced values of $\theta_1$ in all chromophores (MPAR–MPAM12) are authorizing the planarity in the optimized geometries gained by the acceptor moieties. The significant change in $\theta_1$ as compared to $\theta_1$ in all chromophores (MPAR–MPAM12) are authorizing the planarity in the optimized geometries gained by the acceptor moieties. The significant change in $\theta_1$ as compared to $\theta_1$ is due to the possibility of free rotation in less sterically restricted acceptor moieties attached to the thiophene bridge.

2.2. Quantum Mechanical Descriptors. Chromophore orbitals with the highest occupied (HOMO) and lowest unoccupied (LUMO) energies have a considerable effect on the charge transport, electronic, and absorption attributes. Charge transport and electronic density distribution patterns are characterized by Frontier molecular orbitals (FMOs). A molecule accompanied by a small band gap is highly polarizable and has low kinetic stability but great chemical reactivity (i.e., it is a soft molecule).
To study the effect of the thiophene moiety and different end-capped acceptors on photophysical properties of studied molecules MPAR and MPAM1–MPAM12 HOMO and LUMO energy levels along with their band gaps ($E_g$) are studied at elected functionals and their values are illustrated in Table 2. MPAR reflects an $E_g$ of 2.54 eV with HOMO and LUMO energy levels of $-5.01$ and $-2.47$ eV, respectively. HOMO and LUMO levels of all designed chromophores (MPAM1–MPAM12) are low lying in energy as compared to MPAR. Among chromophores (MPAM1–MPAM6) in which additional modification is executed on both side terminals of reference, MPAM5 (2.07 eV) and MPAM6 (2.38 eV) disclosed narrow $E_g$. All chromophores (MPAM7–MPAM12) in which morphological transformation is implemented on our model molecule revealed a reduced band gap ($E_g$) within the limit of 1.78–2.45 eV, as displayed in Figure 4. A significant decrease in $E_g$ is attributable to strong electron-withdrawing end-capped groups that shift the electron density from HOMO to LUMO. MPAM12 has conveyed the lowest value of 1.78 eV owing to the cyano group-containing strong acceptor moiety (2-ethylidene-1,3-dioxo-2,3-dihydro-1H-indene-5,6-dicarbonitrile). Hence, it is inferred that end-capped alteration on one side terminal of MPAR is the best strategy to acquire excellent photophysical properties.

FMO plots (Figure S2 in the Supporting Information) and individual energy levels of studied molecules (MPAR–MPAM12) are shown in Figure 5. The red and green color symbolizes the positive and negative charge, respectively. The donor unit is symbolized by HOMO and the acceptor is represented by LUMO. HOMO electronic density of the model molecule (MPAR) is completely populated on the central core and TPA donor portion, while LUMO is inhabited on the electron-withdrawing central core.

The FMO pattern of MPAM1–MPAM6 seems to be similar. In these molecules, HOMOs are majorly populated on the central acceptor core and TPA donor fragment and partially concentrated on the bridge moiety, while LUMOs are assembled partially on the TPA donor moiety, completely on the bridge and end-capped acceptors. In the case of MPAM5, LUMO is colonized utterly on the central core, minorly on the donor, bridge, and acceptor moiety. FMO distribution of MPAM7–MPAM12 is quite similar in such a way that their HOMOs are inhabited completely on the central core and TPA unit, while LUMOs are populated entirely on bridge and acceptor units, partially on thiophene bridge units. HOMO electronic cloud is primarily diffused on the donor moiety, and LUMO electronic cloud is scattered on thiophene bridge and acceptor units.

2.3. Ionization Potential and Electron Affinity. Trademark boundaries to investigate the charge transmission nature are ionization potential (IP) and electron affinity (EA). Both IP and EA are equivoically associated with one another. Proficient charge transfer is characterized by chromophores exhibiting the greater value of EA and lower IP. Chromophores with electron-donating groups have low IP because of the destabilization of the HOMO energy level, hence accelerating the easy removal of electrons during charge transfer. Contrarily, molecules accompanied by electron-withdrawing groups possess a high value of IP due to stabilization of HOMO. IP and EA values of all investigated molecules (MAPR and MPAM1–MPAM12) evaluated using eqs 1 and 2 are summarized in Table 2.

\[
IP = [E_0^+ - E_0]
\]
Among all designed molecules, MPAM8 and MPAM9 possess low IPs of 5.90 eV each because of their high-lying HOMO levels. The highest IP (6.59 eV) is exhibited by MPAM6 credited to its low energy HOMO. As all newly architecture molecules are tailored by acceptor moiety modification, they reveal a high value of EA as compared to reference MPAR, thus promoting charge transfer, as illustrated in Table 2.

2.4. Absorption Profile. Harvesting and absorption of light energy are the central parameters that have gained

![Figure 2. UV−vis spectra of MPAR at five different DFT functionals using 6-311G (d,p) in (a) gas (b) DCM.](image)

![Figure 3. Comparative analysis of absorption in the bar chart of reference (MPAR) at five different DFT functionals.](image)

### Scheme 1. Calculated Bond Angle ($\theta$) and Bond Length ($d$) of Molecules

\[
EA = [E_E - E_0]
\]

### Table 1. Computed Dihedral Angle ($\theta$) and Bond Length ($d$) of Molecules (MPAR−MPAM12)

| molecules | $\theta_1$ (deg) | $\theta_2$ (deg) | $d_1$ (Å) | $d_2$ (Å) |
|-----------|------------------|------------------|------------|------------|
| MPAR      | 61.34            | 0.34             | 1.36       | 1.41       |
| MPAM1     | 24.48            | 0.64             | 1.46       | 1.42       |
| MPAM2     | 24.74            | 0.61             | 1.46       | 1.42       |
| MPAM3     | 23.98            | 0.60             | 1.46       | 1.43       |
| MPAM4     | 24.50            | 0.88             | 1.46       | 1.42       |
| MPAM5     | 25.16            | 0.90             | 1.46       | 1.43       |
| MPAM6     | 23.42            | 0.72             | 1.45       | 1.41       |
| MPAM7     | 24.28            | 0.65             | 1.46       | 1.42       |
| MPAM8     | 24.60            | 0.61             | 1.46       | 1.42       |
| MPAM9     | 23.84            | 0.64             | 1.46       | 1.43       |
| MPAM10    | 25.08            | 1.02             | 1.46       | 1.42       |
| MPAM11    | 25.09            | 0.87             | 1.46       | 1.43       |
| MPAM12    | 22.99            | 0.69             | 1.45       | 1.41       |
The absorption profile of newly engineered molecules (MPAM1–MPAM12) was computed via the selected optimal DFT functional in the gaseous (MPAR) and solvent [dichloromethane (DCM)] phase as expressed in Figure 6a and Figure 6b. The employment of solvent has red-shifted the $\lambda_{\text{max}}$ owing to the stabilization of delocalized $\pi$ electrons. In the present investigation, the absorption profile by employing the TD-DFT calculations in the IEFPCM model has been pictured as the results have been reported in Tables 3 and 4, respectively.

The absorption profile illustrates that among all newly devised molecules, MPAM6, MPAM7, and MPAM12 are accompanied by a higher $\lambda_{\text{max}}$ value than the model molecule (MPAR) in DCM. The $\lambda_{\text{max}}$ value is in strong alliance with the band gap. The lower the band gap, the more will be the $\lambda_{\text{max}}$ value. The absorption profile supports the fact that MPAM6 and MPAM12 are accompanied by cyano-containing (2-ethylidene-1,3-dioxo-2,3-dihydro-1H-indene-5,6-dicarbonitrile) strong electron-pulling moieties. Cyano and carbonyl groups serve as electron-capturing moieties to facilitate the charge transmission from donor to acceptor.

Table 2. Computed HOMO and LUMO Energies, Band Gap ($E_g$), Ionization Potential, and Electron Affinity

| molecules | HOMO (eV) | LUMO (eV) | $E_g$ (eV) | IP (eV) | EA (eV) |
|-----------|-----------|-----------|-----------|---------|---------|
| MPAR      | $-5.01$   | $-2.47$   | $2.54$    | $5.68$  | $1.45$  |
| MPAM1     | $-5.73$   | $-3.11$   | $2.62$    | $6.26$  | $2.64$  |
| MPAM2     | $-6.03$   | $-3.20$   | $2.83$    | $6.12$  | $2.43$  |
| MPAM3     | $-5.85$   | $-3.06$   | $2.79$    | $6.13$  | $2.48$  |
| MPAM4     | $-6.18$   | $-3.55$   | $2.63$    | $6.55$  | $2.79$  |
| MPAM5     | $-5.92$   | $-3.85$   | $2.07$    | $6.30$  | $2.43$  |
| MPAM6     | $-6.35$   | $-3.97$   | $2.38$    | $6.59$  | $3.23$  |
| MPAM7     | $-5.20$   | $-3.05$   | $2.15$    | $5.96$  | $2.33$  |
| MPAM8     | $-5.17$   | $-2.86$   | $2.31$    | $5.90$  | $2.17$  |
| MPAM9     | $-5.19$   | $-2.89$   | $2.30$    | $5.90$  | $2.20$  |
| MPAM10    | $-5.37$   | $-3.24$   | $2.13$    | $6.07$  | $2.42$  |
| MPAM11    | $-5.33$   | $-2.88$   | $2.45$    | $5.97$  | $2.14$  |
| MPAM12    | $-5.38$   | $-3.60$   | $1.78$    | $6.09$  | $2.88$  |

Cyano, fluoro, and carbonyl groups also escalate the molecular conjugation and push the absorption toward a longer wavelength by attaching to the conjugated framework of the molecule. MPAM7 has also displayed a higher $\lambda_{\text{cal}}$ value than the model molecule (MPAR) due to the presence of carbonyl- and fluoro-containing (2-ethylidene-5,6-difluoro-2H-indene-1,3-dione) strong electron-pulling moieties. Cyanide, fluorine, and carbonyl groups augment the photovoltaic activity of the device by lowering the energy of FMOs. From the absorption profile, it is overall illustrated that molecules (MPAM7–MPAM12) accompanied by electron-withdrawing moieties on one side terminals exhibit a higher $\lambda_{\text{max}}$ value and lower band gaps as compared to molecules (MPAM1–MPAM6) having electron-withdrawing moieties on both side terminals, as displayed in Figure 7.

In the present quantum simulation, the first excitation energy has been calculated using the selected functional in both gas and solvent medium as the results have been displayed in Figure 8. The first excitation energy is the amount of energy necessary for the electrons to excite from the ground to the first excited state. Excitation energy is in direct alliance with the band gap energy. The lower the band gap value, the lower will be the excitation energy and more considerable will be the excitation of electrons from the ground to the excited state. More excitation of electrons leads to efficient charge transfer and hence results in intensified photocurrent generation.

In the current report, all reported molecules have manifested a higher value of excitation energy in the gas phase as compared to the solvent phase, as displayed in Figure 8. The higher values of excitation energy of molecules in the gas phase are advocating the fact that freshly planned molecules have greater miscibility in the solvent (DCM) and more charge transfer, hence proving that all reported molecules are solution-processable molecules responsible for the augmented photocurrent generation.

Another essential technique to examine the optical utility of the investigated compounds is the light-harvesting efficiency (LHE). LHE is computed through the oscillatory strength ($f_i$) value and represents the compound photocurrent response.43

Figure 4. Graphical representation of band gap (a) for MPAR and MPAM1–MPAM6 molecules (b) for MPAR and MPAM7–MPAM12.
LHE is in direct relation with the \( f \) value. Compounds accompanied by large LHE values manifest large photocurrent responses and vice versa. LHE of currently reported structures in both gas and solvent medium has been calculated using eq 3,43 and the results have been summarized in Tables 3 and 4, respectively. A pronounced shift in LHE values of newly devised structures has been observed by structural modifications. Among all reported structures, MPAM1–MPAM6 having structural tailoring at both side ends are accompanied by higher \( f \) and LHE values, which is attributed to their augmented photocurrent generation.

2.5. Quantum Chemical Parameters. To scrutinize the chemical reactivity and kinetic stability of newly engineered molecules, different chemical parameters have been calculated and results have been summarized in Table 5.

\[
\mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2}
\]

Equation 444 has been used for calculating chemical potential. Chemical potential describes the electronic cloud
escaping capability. The freshly designed molecules are accompanied by higher values of negative chemical potential indicating that they are highly reactive and stable compounds hence cannot decompose easily. The designed molecules
exhibit a greater value of chemical potential than PC_{61}BM indicating that they have a greater ability to donate electrons.

Chemical hardness ($\eta$) = \( \frac{(E_{\text{LUMO}} - E_{\text{HOMO}})}{2} \)  \hspace{1cm} (5)

Chemical softness ($S$) = \( \frac{1}{\eta} \)  \hspace{1cm} (6)

Chemical hardness and softness values calculated using eqs 5 and 6, respectively, demonstrate that among all reported molecules, MPAM5–MPAM12 are soft molecules accompanied by the lowest band gaps and enhanced chemical reactivity, while MPAM1–MPAM4 molecules are relatively hard molecules accompanied by enhanced kinetic stability owing to their increased band gaps than the reference (MPAR).

Electronegativity ($\chi$) = \( -\frac{(E_{\text{HOMO}} + E_{\text{LUMO}})}{2} \)  \hspace{1cm} (7)

Electrophilicity index ($\omega$) = \( \frac{\chi^2}{2(\eta)} \)  \hspace{1cm} (8)

Electronegativity and electrophilicity index values have been simulated using eqs 7 and 8, respectively. Both are usually correlated and quantitatively explain the electron-accepting nature of molecules. All designed molecules have manifested higher values of the electronegativity and electrophilicity index than the reference (MPAR) advocating the fact that newly
designed molecules are accompanied by strong electron-withdrawing moieties. All reported molecules are accompanied by low values of the electronegativity and electrophilicity index as compared to PC$_{61}$BM indicating that they have less ability to attract electrons from PC$_{61}$BM and behave as an electron donor.

The total amount of charge transfer is another parameter to scrutinize the charge-transferring capability of all freshly planned molecules, calculated using eq 9. The summarized results in Table 5 have shown that all newly engineered molecules have a greater ability to transfer charge than the reference (MPAR). Keeping in view the abovementioned discussion, the freshly designed molecules ought to be focused to prepare elite materials for future proficient solar devices.

\[
\text{Total amount of charge transfer} = \Delta N_{\text{max}} = -\frac{\mu}{\eta} \Delta N_{\text{max}} (\text{e}) 
\]

2.6. Density of State Analysis. FMO results have been assured via Mulliken charge distribution. The density of state (DOS) analysis expresses the contribution of the molecular fragment in raising the bonding (HOMO) and antibonding (LUMO) molecular orbitals. DOS calculations also compute the energies of HOMO and LUMO. The DOS simulations were computed at the selected DFT functional for MPAR and MPAM1–MPAM12 and transfigured via PyMolyze 1.1. To study DOS, MPAR is partitioned into donor (red color) and core (green color) sections, while all other designed molecules MPAM1–MPAM12 are fractioned into four segments acceptor, spacer, TPA donor, and core presented by red, green, blue, and pink colors, respectively, in DOS plots, as illustrated in Figure 9. Negative and positive values along the x-axis in DOS diagrams address HOMO and LUMO values, respectively, while the energy difference between them represents band gap.

Table 6 outlines the role of different fragments in devising HOMO and LUMO. In MPAR, HOMO is formed majorly by the contribution of the TPA donor and minorly by the central core, while LUMO is formed mainly by the core which is an acceptor in nature. The contribution of different fragments in the formulation of HOMO and LUMO in MPAM1–MPAM6 is analogous. In these molecules, HOMO is obtained

| molecules | $\mu$ (eV) | $\eta$ (eV) | $S$ (eV) | $\chi$ (eV) | $\omega$ (eV) | $\Delta N_{\text{max}}$ (e) |
|-----------|------------|------------|---------|------------|-------------|-----------------------------|
| MPAR      | -3.74      | 1.27       | 0.79    | 3.74       | 5.51         | 2.94                        |
| MPAM1     | -4.42      | 1.31       | 0.76    | 4.42       | 7.46         | 3.37                        |
| MPAM2     | -4.61      | 1.42       | 0.70    | 4.61       | 7.48         | 3.24                        |
| MPAM3     | -4.46      | 1.40       | 0.71    | 4.46       | 7.30         | 3.19                        |
| MPAM4     | -4.87      | 1.32       | 0.76    | 4.87       | 8.98         | 3.69                        |
| MPAM5     | -4.89      | 1.04       | 0.96    | 4.89       | 11.50        | 4.70                        |
| MPAM6     | -4.86      | 1.19       | 0.84    | 4.86       | 11.19        | 4.08                        |
| MPAM7     | -4.13      | 1.08       | 0.93    | 4.13       | 7.90         | 3.82                        |
| MPAM8     | -4.02      | 1.16       | 0.86    | 4.02       | 6.97         | 3.47                        |
| MPAM9     | -4.04      | 1.15       | 0.87    | 4.04       | 7.10         | 3.51                        |
| MPAM10    | -4.31      | 1.07       | 0.93    | 4.31       | 8.68         | 4.03                        |
| MPAM11    | -4.11      | 1.23       | 0.81    | 4.11       | 6.87         | 3.34                        |
| MPAM12    | -4.49      | 0.89       | 1.12    | 4.49       | 11.33        | 5.04                        |
| PC$_{61}$BM | -4.90      | 1.20       | 0.83    | 4.90       | 10.00        | 4.08                        |
Table 6. Acceptor, Spacer, TPA Donor, and Core Contribution in Raising the HOMO and LUMO of Reference (MPAR) and Designed Chromophores (MPAM1–MPAM12)

| molecules | LUMO = L | acceptor (eV) | spacer (eV) | TPA donor (eV) | core (eV) |
|-----------|----------|---------------|-------------|----------------|-----------|
| MPAR      | H        | 72.5          | 27.5        |                 |           |
|           | L        | 9.8           | 90.2        |                 |           |
| MPAM1     | H        | 5.6           | 9.6         | 55.1           | 29.8      |
|           | L        | 57.7          | 30.0        | 12.3           | 0.0       |
| MPAM2     | H        | 5.9           | 10.5        | 56.3           | 27.3      |
|           | L        | 56.5          | 30.3        | 12.9           | 0.2       |
| MPAM3     | H        | 10.2          | 12.3        | 53.9           | 23.6      |
|           | L        | 55.2          | 25.6        | 12.1           | 7.0       |
| MPAM4     | H        | 4.0           | 7.4         | 51.7           | 36.9      |
|           | L        | 48.5          | 36.8        | 14.6           | 0.1       |
| MPAM5     | H        | 4.5           | 8.9         | 54.5           | 32.0      |
|           | L        | 11.5          | 9.1         | 13.9           | 65.6      |
| MPAM6     | H        | 4.8           | 7.3         | 50.6           | 37.2      |
|           | L        | 62.0          | 27.6        | 10.4           | 0.0       |
| MPAM7     | H        | 0.1           | 0.1         | 79.3           | 20.5      |
|           | L        | 57.7          | 30.0        | 12.3           | 0.0       |
| MPAM8     | H        | 0.1           | 0.2         | 78.3           | 21.4      |
|           | L        | 46.0          | 30.4        | 23.6           | 0.0       |
| MPAM9     | H        | 0.2           | 0.2         | 78.3           | 21.3      |
|           | L        | 60.1          | 27.9        | 11.9           | 0.1       |
| MPAM10    | H        | 0.0           | 0.1         | 80.7           | 19.2      |
|           | L        | 48.7          | 36.9        | 14.4           | 0.0       |
| MPAM11    | H        | 0.1           | 0.1         | 79.1           | 20.7      |
|           | L        | 46.5          | 36.7        | 16.8           | 0.0       |
| MPAM12    | H        | 0.0           | 0.1         | 81.3           | 18.7      |
|           | L        | 62.1          | 27.6        | 13.0           | 0.0       |

predominantly by the TPA donor fragment, partially by core and insignificantly by acceptor and spacer units, while in the formation of LUMO, the end-capped acceptor and thiophene bridge play a significant role. Likewise, in MPAM7–MPAM12, HOMO is obtained by 80% participation of TPA donor fragment and almost negligible contribution of the acceptor and spacer. LUMO is modeled by acceptor and spacer fragments majorly with no significant assistance of the central core.

2.7. Molecular Electrostatic Potential Surface. Charge transfer between donor and acceptor moieties in an excited state has been assessed with the molecular electrostatic potential (MEP) surface.42 In the current study, MEP simulations have been performed at an optimum DFT functional to determine the electrophilic and nucleophilic areas. The electrophilic region is symbolized by the red color, which epitomizes a negative value of electrostatic potential and an abundance of electrons in that region, while the green color transcribes an electrically neutral region, and the blue color symbolizes the positive region only, while the central acceptor core is covered by shades of red representing the negative region having an abundance of electrons. MEP surface plots of studied molecules (MPAM1–MPAM12) manifest that the donor portion is covered by shades of blue (positive region) and end-capped acceptor moieties are covered by shades of red (negative region) advocating their compliance for electrophilic reactivity (readily susceptible to nucleophile attack), as depicted in Figure 10. To sum up, based on colonization of electron density in varying regions, all newly planned molecules being reactive exhibit efficient charge transmission during excitation and can be employed as optimistic candidates for future proficient solar gadgets.

2.8. Transition Density Matrix and Exciton Binding Energy. The most persuasive tool for quantifying the electronic excitation processes (generation, diffusion, recombination, and separation of charges) is the transition density matrix (TDM). TDM demonstrates the quantum geometry of molecules in the excited state. TDM figures out the interrelation between donating and accepting moieties during excitation.

TDM analysis of MPAR and currently aimed MPAM1–MPAM12 has been carried out by employing the selected hybrid DFT functional. Figure 12 displays the pictorial view of the model (MPAR) along with devised molecules (MPAM1–MPAM12). MPAR has been divided into two components, core (C) and donor (D), while the devised molecules (MPAM1–MPAM12) have been sequestered into four fractions, namely, core (C), donor (D), bridge (B), and acceptor (A). In TDM plots, atom numbers are displayed on the bottom and left axis, while electron density in the molecule is located on the right axis.

Because of the insignificant contribution in transitions, hydrogen atoms have been ignored. In the model molecule (MPAR), the charge consistency can be seen in the donor and core fraction. In the devised molecules (MPAM1–MPAM12), uniform distribution of charge along with charge coherency in the acceptor region can be seen accompanied by the salutary diagonal and off-diagonal charge transfer. The TDM plots in Figure 11 demonstrate that the excellent charge transmission from donor to acceptor via the bridge has been seen expressing that freshly planned molecules are accompanied by less electron coupling exhibiting the greater exciton dissociation potential. The major electronic transitions of the reference molecule (MPAR) and the newly devised molecules (MPAM1–MPAM12) in the gas phase and DCM have been displayed in Tables 3 and 4, respectively.

Exciton binding energy is another parameter to scrutinize the charge transmission potential. In the current study, the binding energies of all molecules have been calculated in the gaseous and solvent phase using eq 10 and results have been reported in Tables 3 and 4, respectively.

\[ E_b = E_g - E_x \]  

(10)

\[ E_b \] is the binding energy, \( E_g \) represents the band gap, and \( E_x \) symbolizes the first excitation energy in eq 13. From the summarized results of binding energy, it is illustrated that molecules (MPAM7–MPAM12) accompanied by electron-withdrawing moieties on one side terminals of MPAR are accompanied by lower values of binding energy in gas and DCM as compared to molecules (MPAM1–MPAM6) having electron-withdrawing moieties on both side terminals of MPAR, thus endorsing greater exciton dissociation potential, leading to efficient charge transfer.

Keeping in view the TDM and exciton binding energy analysis, the devised moieties have manifested improved charge transmission from the donor fragment to acceptor group via
Figure 10. MEP surface plots of reference (MPAR) and devised molecules (MPAM1–MPAM12).

Figure 11. TDM plots of reference (MPAR) and devised molecules (MPAM1–MPAM12).
Dipole Moment (µ).

Dipole moment is a crucial assumption in calculating the solubility of chromophores in the organic solvent. The larger the dipole moment, the greater is the solubility. The solubility of the molecule is strongly correlated to the smooth structure of the donor−acceptor blend layer in OSCs. Insights into charge transfer efficiency are revealed by the smooth morphology of the thin film, which is the distinctive trait of effective OSCs.52,53

The dipole moment of the investigated molecules (MPAR−MPAM12) is theoretically evaluated at the elected DFT functional. Summarized values of the dipole moment in the ground state (µg), the excited state (µe), and the difference between them (Δµ) are presented in Table 7, and graphical representation of the dipole moment in the ground state, as well as excited state, is pictured in Figure 12.

Table 7. Computed Dipole Moment for MPAR−MPAM12 in the Ground State (µg), Excited State (µe), and Difference between Them (Δµ)

| molecules | µg (D) | µe (D) | Δµ (D) |
|-----------|--------|--------|--------|
| MPAR      | 3.52   | 4.98   | 1.46   |
| MPAM1     | 2.71   | 4.13   | 1.42   |
| MPAM2     | 3.00   | 4.39   | 1.39   |
| MPAM3     | 3.67   | 5.41   | 1.74   |
| MPAM4     | 2.74   | 4.40   | 1.66   |
| MPAM5     | 6.41   | 8.52   | 2.11   |
| MPAM6     | 2.49   | 4.04   | 1.55   |
| MPAM7     | 10.25  | 10.93  | 0.68   |
| MPAM8     | 6.50   | 7.26   | 0.76   |
| MPAM9     | 11.03  | 12.91  | 1.88   |
| MPAM10    | 16.25  | 17.85  | 1.60   |
| MPAM11    | 10.43  | 12.03  | 1.60   |
| MPAM12    | 19.21  | 20.74  | 1.53   |

µg is calculated in DCM solvent to project the solubility of studied molecules. MPAR reveals a µg and µe of 3.52 and 4.98 D, respectively. In MPAM1−MPAM6, where structural modification was performed on both end terminals of MPAR, elevated µg is observed for MPAM3 (3.67 D) and MPAM5 (6.41 D) when contrasted with our model molecule (MPAR). While molecules in which structural adjustments were accomplished on one end terminal of reference, all molecules (MPAM7−MPAM12) demonstrate a remarkable increase in µg and their values lie in the range of 6.50 to 19.21 D. µe assessed in the solvent phase shows that all molecules (MPAR−MPAM12) in DCM have evident intensified dipole moment. A significant increase in the dipole moment is certified with an increase in solubility of molecules in DCM solvent and the presence of polar regions in their structures.

MPAM1, MPAM2, MPAM4, and MPAM6 show lower µe among all designed chromophores (MPAM1−MPAM12) attributing to the greater symmetry in molecules. The highest value of µe is revealed by MPAM12 because of its more solubility in DCM solvent which facilitates self-assembly, reduces exciton recombination, and aids in multilayer fabrication. The abovementioned discussion explores that the freshly designed molecules (MPAM1−MPAM12) are solution-processable, ought to be focused to contrive elite charge-transferring candidates for upcoming solar gadgets.

Reorganization Energy (RE) and Charge Transfer Integral.

The most probable metric to quantify the charge carrier transport characteristics is reorganization energy (RE).54 It is defined as the energy required to modify and deform the structural properties of the reactant and its integrated solvent molecules.55 The external reorganization has been overlooked since it is hard to quantify.

The charge transfer alliance between the donor unit and the acceptor unit in the respective molecule is evaluated via internal reorganizational energy. It varies inversely with the charge transmission rate. The lower the value of internal reorganizational energy, the higher will be the charge transmission rate. The structure of the anion and cation plays a crucial role in determining the probability of electron transfer from the donor and hole transfer in the acceptor, respectively. In this current investigation, the focus is on the internal reorganization energy. It is statistically evaluated using eqs 11 and 12.

\[
\lambda_e = [E^0_+ - E^0_-] + [E_0^+ - E_{-}^-] \quad (11)
\]
\[ \lambda_h = [E_0^+ - E_0^-] + [E_{\text{opt}}^+ - E_{\text{opt}}^-] \]  

Table 8. Reorganization Energy of Electron (\(\lambda_e\)) and Hole (\(\lambda_h\)), and Transfer Integral of Electrons (\(t_e\)) and Hole (\(t_h\)) of MPAR and MPAM1–MPAM12

| molecules | \(\lambda_e\) (eV) | \(\lambda_h\) (eV) | \(t_e\) (eV) | \(t_h\) (eV) |
|-----------|-----------------|-----------------|-------------|-------------|
| MPAR      | 0.0160913       | 0.0071995       | 0.705       | 0.09        |
| MPAM1     | 0.0042799       | 0.0077049       | -0.065      | 0.075       |
| MPAM2     | 0.0041573       | 0.0068533       | 0.15        | -0.14       |
| MPAM3     | 0.0060241       | 0.0047178       | 0.06        | -0.05       |
| MPAM4     | 0.0042479       | 0.0095449       | 0.125       | 0.005       |
| MPAM5     | 0.0052275       | 0.0080696       | 0.465       | 0.005       |
| MPAM6     | 0.0028063       | 0.0099475       | 0.15        | -0.05       |
| MPAM7     | 0.0072771       | 0.0082084       | 0.055       | 0.25        |
| MPAM8     | 0.0060033       | 0.0076755       | 0.05        | 0.215       |
| MPAM9     | 0.0064652       | 0.0068754       | 0.045       | 0.21        |
| MPAM10    | 0.0066191       | 0.0086163       | 0.01        | 0.255       |
| MPAM11    | 0.0082533       | 0.0082651       | 0.06        | 0.195       |
| MPAM12    | 0.0058227       | 0.0087601       | 0.06        | 0.275       |

Values of \(\lambda_e\) than MPAR manifest higher mobilities of an electron from donor to acceptor moiety. The findings of Table 8 validate that all our newly engineered molecules (MPAM1–MPAM12) evince lower \(\lambda_e\) when equated with our model molecule MPAR (0.0160913 eV). The theoretically calculated lowest \(\lambda_e\) is procured for MPAM6 (0.0028063 eV) which is conceived by end-capped acceptor modification on both side terminals of our model molecule MPAR. Likewise, computationally computed \(\lambda_h\) of designed molecules MPAM1–MPAM12 covers a range from 0.0047178 to 0.0108845 eV. Among all designed molecules, MPAM2 (0.0068533 eV), MPAM3 (0.0047178 eV), and MPAM9 (0.0068754 eV) reflect lower values of \(\lambda_h\) when contrasted to reference MPAR (0.0071995 eV) which are accredited to the acceptor moieties that assist hole transport. It is deduced that our designed molecules are empowering charge-transporting materials for future proficient solar devices.  

Another factor affecting the charge rate in the Marcus equation is the transfer integral of electrons and holes. The charge transfer integral is the internal molecular stacking of modeled molecules. It represents the ease of charge transfer. More values of charge integral ensure fewer abnormal states in the way to charge mobility. The charge integral values were calculated using following eqs 13 and 14:  

\[ t_e = \frac{1}{2} (E_{H_1} - E_{H_{-1}}) \]  

\[ t_h = \frac{1}{2} (E_{L_{+1}} - E_L) \]

The summarized calculated values of transfer integral of electrons \((t_e)\) and hole \((t_h)\) have been expressed in Table 8. Among all, MPAM7–MPAM12 have displayed higher hole transfer integral values (0.195–0.275 eV), as displayed in Figure 14, advocating their enhanced hole mobility rate and empowering their potential use as HTMs for future elite PSCs.  

Figure 13. Graphical view of reorganization energy of electron (\(\lambda_e\)) and hole (\(\lambda_h\)) (a) for MPAR and MPAM1–MPAM6 molecules (b) for MPAR and MPAM7–MPAM12.
In eq 15, $e$ symbolizes the charge on molecule and 0.3 represents a constant computed from voltage drop. PC$_{61}$BM has been used as an acceptor. The HOMO and LUMO of PC$_{61}$BM have been explored as $-6.1$ and $-3.7$ eV, respectively. The low-energy LUMO of the acceptor computes the highest $V_{OC}$. Figure 15 manifests $V_{OC}$ of MPAR and MPAM1–MPAM12 with PC$_{61}$BM. In this current study, MPAM1–MPAM12 are donors, which is why their HOMO has been scaled with the LUMO of PC$_{61}$BM.

The $V_{OC}$ of MPAR has been explored as 1.01 eV. A pronounced shift in $V_{OC}$ values has been manifested by tailoring the end-capped acceptors of the model molecule (MPAR), as summarized in Table 9. The newly devised chromophores (MPAM1–MPAM12) have shown high open-circuit voltage than the MPAR owing to their low-lying HOMO advocating the fact that all reported molecules have great potential to be used as efficient HTMs. Briefly, the newly
has been estimated using eq 18. The estimated values of PCE (MPAM1–MPAM12) have been displayed in Table 9. All newly engineered molecules (MPAR) and Newly Engineered Molecules (MPAM1–MPAM12) have displayed higher FF endorses the functioning ability and can be used as the aristocratic materials for future elite solar devices.

### 2.12. Fill Factor. To calculate the PCE of solar devices, the fill factor (FF) is an integral parameter. The FF has been calculated using eq 16.57

\[
FF = \left( \frac{\frac{eV}{k_BT}}{\frac{eV}{k_BT} + 1} \right) \ln \left( \frac{\frac{eV}{k_BT}}{\frac{eV}{k_BT} + 1} + 0.72 \right)
\]

In eq 16, \(V\) is open-circuit voltage, \(K_B\) is the Boltzmann constant, \(T\) is the temperature at 298 K, and \(e\) is an elementary charge (1) on the molecule. The term \(\frac{eV}{k_BT}\) is normalized voltage. The summarized results of the calculated FF have been displayed in Table 9. All newly engineered molecules (MPAM1–MPAM12) have manifested a higher FF value than the reference (MPAR). The higher FF endorses the effectiveness of freshly engineered structures for future elite solar gadgets.

### 2.13. Power Conversion Efficiency. PCE of solar devices has been estimated using eq 18.59 The estimated values of PCE values of all reported molecules have been displayed in Table 10.

\[
PCE = \frac{J_{SC} \cdot V_{OC} \cdot FF}{P_{in}}
\]

In eq 17, the short circuit current value \((J_{SC})\) \((23.23\ mA\ cm^{-2})\) has been taken from the reference paper and has been assumed for all freshly planned molecules for estimating their PCE. The \(P_{in}\) is the power of incident rays on the solar cells during the estimation of PCE which is commonly fixed at AM 1.5G, 100 mW cm\(^{-2}\).

The pictographic representation of the estimated PCE values has been manifested in Figure 16, illustrating that all newly contrived molecules (MPAM1–MPAM12) have explored enhanced PCE than the reference molecule (MPAR) due to structural modification by the introduction of thiophene-bridged end-capped strong electron-pulling moieties.

In a nutshell, the thiophene-bridged end-capped acceptor alteration tactic has been proved compelling in providing the new gateway for boosting the optoelectronic properties and newly customized molecules should be targeted to contrive future proficient solar devices.

### 3. CONCLUSIONS

The current study relies on offering donor contributors for OSCs and productive HTMs for PSCs. Selected MPW1PW91/6-311G has been used for the computational simulations in the current study. As a result, the newly designed molecules (MPAM1–MPAM12) have manifested impressive outcomes. MPAM5–MPAM12 displayed reduced band gaps ranging from 1.78 to 2.45 eV and then MPAR (2.54 eV). MPAM7 (600 nm), MPAM6 (651 nm), and MPAM12 (639 nm) are accompanied by higher \(\Delta_{max}\) values in DCM as compared to MPAR (596 nm). The newly planned molecules (MPAM7–MPAM12) are enriched with a higher dipole moment varying from 7.26 to 20.74 D in DCM than the ground state addressing their good solubility and less charge recombination. The RE values indicate that newly engineered molecules exhibit paramount charge mobility than reference. Among all, MPAM7–MPAM12 displayed higher hole transfer integral values (0.195–0.275 eV) advocating their enhanced hole mobility rate and empowering their potential use as HTMs for future elite PSCs. Moreover, all newly planned molecules when scaled with the PC61BM acceptor displayed higher \(V_{OC}\) values 1.17 to 2.18 eV than MPAR (1.01 eV) which suggested that these donor contributors hold a compelling position in achieving escalating operational efficiency. All designed molecules are accompanied by a higher estimated PCE (24.78–47.86%) than the reference (MPAR) proving their effectiveness for upcoming solar devices. Thus, the thiophene-bridged end-capped acceptor-alteration strategy is a promising way to design optimistic photovoltaic materials. Therefore, all newly designed molecules might potentially contribute in improving the device’s functioning ability and can be used as the aristocratic materials in planning future elite solar devices.

### 4. COMPUTATIONAL DETAILS

All ground-state geometry optimization of MPAR and MPAM1–MPAM12 was executed using Gaussian 09 software package,60 while GaussView 5.0.8 program61 was used for
drawing structures and presentation of results. The DFT computations were accomplished for auxiliary streamlining of MPAR reference at B3LYP, CAM-B3LYP, PBE0, MPW1PW91, and ωB97XD functionals in alliance with the 6-311G (d,p) basis set. Low-lying excited state’s characteristics were assessed at the ground state applying TD-DFT. The accomplished $\lambda_{\text{max}}$ of MPAR from four different functionals was certified with the experimental value given in the literature to validate the hypothetical strategy. The MPW1PW91 functional manifested precise compromise between experimentally (532 nm) and theoretically (596 nm) determined absorption values and consequently presented a realistic argument for its manipulation in quantum chemical computations. All designed molecules (MPAM1–MPAM12) were geometrically optimized at the MPW1PW91/6311G (d,p) level of theory. DCM solvent impact has been simulated using the solvation model IEFPCM. The $\lambda_{\text{max}}$ of MPAR and MPAM1–MPAM12 was computed both in gas and solvent phases. Computational transfiguration of $\lambda_{\text{max}}$ was performed using the Swizard program. Collectively, $\lambda_{\text{max}}$ values were plotted via Origin 6.0 program. FMO analysis, DOS calculations, TDM examination, reorganization energy, and dipole moment simulations were computationally accomplished by the optimal theoretical DFT-selected functional. To analyze the contribution of molecular fragments, DOS files were pictured via PyMOLyze 1.1 software. Estimation of electron densities and electronic transitions was executed using the Multiwfn 3.7 software. To model the electron and hole transfer rate, eq 1 is the key parameter. Total reorganization energy is the sum of internal ($\lambda_i$) and external reorganization energy ($\lambda_e$).

$$\lambda = \lambda_i + \lambda_e$$

(18)

Inner-sphere and outer-sphere reorganization energies peak for alteration within the structure of molecules and external environment modification during the charge transport, respectively. To model the changes in cationic and anionic geometry of reference and newly devised molecules, the focus is on the $\lambda_i$. The $\lambda_e$ has been neglected in the present investigation. The mobility rate of the electron ($\lambda_e$) and hole ($\lambda_h$) was computed using subsequent eqs 11 and 12.

## ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05504.

Comparative analysis of absorption in the bar chart and Cartesian coordinates (PDF)

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### Notes

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REFERENCES

(1) Kumaresan, P.; Vegiraju, S.; Ezhumalai, Y.; Yau, S.; Kim, C.; Lee, W.-H.; Chen, M.-C. Fused-thieno-based materials for organic photovoltaics and dye-sensitized solar cells. Polymers 2014, 6, 2645–2669.

(2) Council, W. E. World Energy Resources 2013 Survey; World Energy Council, 2013; pp 1–468.

(3) Ans, M.; Manzoor, F.; Ayub, K.; Nawaz, F.; Iqbal, J. Designing dithienothiophene (DTT)-based donor materials with efficient photovoltaic parameters for organic solar cells. J. Mol. Model. 2019, 25, 222.

(4) Qarony, W.; Hossain, M. I.; Hossain, M. K.; Uddin, M. J.; Haque, A.; Saad, A. R.; Tsang, Y. H. Efficient amorphous silicon solar cells: characterization, optimization, and optical loss analysis. Results Phys. 2017, 7, 4287–4293.

(5) Ishikawa, R.; Shirai, H.; Ueno, K. Nat. Photonics 2012, 6, 153.

(6) Bhogaita, M.; Shukla, A. D.; Nalini, R. P. Recent advances in hybrid solar cells based on natural dye extracts from Indian plant pigments as sensizers. Sol. Energy 2016, 137, 212–224.

(7) Lu, L.; Zheng, T.; Wu, Q.; Schneider, A. M.; Zhao, D.; Yu, L. Recent advances in bulk heterojunction polymer solar cells. Chem. Rev. 2015, 115, 12666–12731.

(8) (a) Yu, J.; Zheng, Y.; Huang, J. Towards High Performance Organic Photovoltaic Cells: A Review of Recent Development in Organic Photovoltaics. Polymers 2014, 6, 2473–2509. (b) Lu, L.; Zheng, T.; Wu, Q.; Schneider, A. M.; Zhao, D.; Yu, L. Recent Advances in Bulk Heterojunction Polymer Solar Cells. Chem. Rev. 2015, 115, 12666–12731.

(9) Ahmed, S.; Kalita, D. J. End-capped group manipulation of non-fullerene acceptors for efficient organic photovoltaic solar cells: a DFT study. Phys. Chem. Chem. Phys. 2020, 22, 23586–23596.

(10) He, Y.; Li, Y. Fullerene derivative acceptors for high performance polymer solar cells. Phys. Chem. Chem. Phys. 2011, 13, 1970–1983.

(11) Ancil, A.; Babbitt, C. W.; Raffaelle, R. P.; Landi, B. J. Material and energy intensity of fullerene production. Environ. Sci. Technol. 2011, 45, 2333–2339.

(12) Liu, T.; Guo, Y.; Yi, Y.; Huo, L.; Xue, X.; Sun, X.; Fu, H.; Xiong, W.; Meng, D.; Wang, Z.; Liu, F.; Russell, T. P.; Sun, Y. Ternary Organic Solar Cells Based on Two Compatibly Non-fullerene Acceptors with Power Conversion Efficiency >10%. Adv. Mater. 2016, 28, 10008–10105.

(13) Zhang, J.; Tan, H. S.; Guo, X.; Facchetti, A.; Yan, H. Material insights and challenges for non-fullerene organic solar cells based on small molecular acceptors. Nat. Energy 2018, 3, 720–731.

(14) Wang, X.; Chen, H.; Ran, A.-R.; Luo, L.; Chan, P. P.; Tham, C. C.; Chang, R. T.; Mannil, S. S.; Cheung, C. Y.; Heng, P.-A. Towards multi-center glaucoma OCT image screening with semi-supervised joint structure and function multi-task learning. Med. Image Anal. 2020, 63, 101695.

(15) Liu, T.; Ma, R.; Luo, Z.; Guo, Y.; Zhang, G.; Xiao, Y.; Yang, T.; Chen, Y.; Li, G.; Yi, Y.; Lu, X.; Yan, H.; Tang, B. Concurrent improvement in JSC and VOC in high-efficiency ternary organic solar cells enabled by a red-absorbing small-molecule acceptor with a high LUMO level. Energy Environ. Sci. 2020, 13, 2115–2123.

(16) Zhan, L.; Li, S.; Lau, T.-K.; Cui, Y.; Lu, X.; Shi, M.; Li, C.-Z.; Li, H.; Hou, J.; Chen, H. Over 17% efficiency ternary organic solar cells enabled by two non-fullerene acceptors working in an alloy-like model. Energy Environ. Sci. 2020, 13, 635–645.
fluorinated terphenyls and theoretical prediction of their third-order nonlinear optical response. *RSC Adv.* 2021, 11, 7766–7778.

(35) Ashraf, A.; Khalid, M.; Tahir, M. N.; Yaqub, M.; Naseer, M. M.; Kamal, G. M.; Saifullah, B.; Braga, A. A. C.; Shafiq, Z.; Rauf, W. A facile and concise route to (hydroxybenzoyl) pyrido [2, 3-d] pyrimidine heterocycle derivatives: synthesis, and structural, spectral, and computational exploration. *RSC Adv.* 2019, 9, 34567–34580.

(36) Ans, M.; Iqbal, J.; Bhatti, I. A.; Ayub, K. Designing dithienonaphthalene based acceptor materials with promising photovoltaic parameters for organic solar cells. *RSC Adv.* 2019, 9, 34496–34505.

(37) Zahid, S.; Rasool, A.; Ans, M.; Yaseen, M.; Iqbal, J. Quantum Chemical Approach of Donor–π-Acceptor Based Arylborane–Arylamine Macrocycles with Outstanding Photovoltaic Properties Toward High-Performance Organic Solar Cells. *Energy Fuels* 2021, 35, 15018.

(38) Khan, M. U.; Iqbal, J.; Khalid, M.; Hussain, R.; Braga, A. A. C.; Hussain, M.; Muhammad, S. Designing triazatruxene-based donor materials with promising photovoltaic parameters for organic solar cells. *RSC Adv.* 2019, 9, 26402–26418.

(39) Hussain, R.; Khan, M. U.; Meebbho, M. Y.; Khalid, M.; Iqbal, J.; Ayub, K.; Adnan, M.; Ahmed, M.; Atiq, K.; Mahmood, K. Enhancement in Photovoltaic Properties of N,N-diethylaniline based Donor Materials by Bridging Core Modifications for Efficient Solar Cells. *ChemistrySelect* 2020, 5, 5022–5034.

(40) Ullah, F.; Kosar, N.; Ali, A.; Maria, T.; Mahmood, T.; Ayub, K. Design of novel inorganic alkali earth metal doped aluminum nitride complexes (AEM@Al12N12) with high chemical stability, improved electronic properties and large nonlinear optical response. *Optik* 2020, 207, 167392.

(41) Habibpour, R.; Vaziri, R. Investigation of structural and electronic properties of small Au n Cu m (n+ m ≤ 5) nano-clusters for Oxygen adsorption. *Int. J. Nano Dimens.* 2016, 7, 208–224.

(42) Hachi, M.; Slimi, A.; Fitri, A.; ElKhattabi, S.; Benjelloun, A. T.; Benzakour, S.; Mcharfi, M. New small organic molecules based on quinacridone based compounds through various modifications. *CrystEngComm* 2021, 23, 388–398.

(43) Ans, M.; Iqbal, J. Theoretical and computational study on electronic effect caused by thiourea derivatives. *RSC Adv.* 2021, 10, 13299–13307.

(44) Padmanabhan, J.; Parthasarathi, R.; Subramanian, V.; Chattaraj, P. K. Electrophilicity-based charge transfer descriptor. *J. Phys. Chem. A* 2007, 111, 1358–1361.

(45) Vaziri, R.; Vaziri, K.; Bener, E. J.; Bickelhaupt, F. M. Voronoi deformation density (VDD) charges: A theoretical and computational study. *J. Phys. Chem. B* 2007, 111, 1358–1361.

(46) Bonilla, C.; Rana, S.; Ayub, K. Nonlinear optical and electronic properties of CF3-Ni, and F3 substituted C 20 fullerene: A quantum-chemical study. *Mater. Res. Bull.* 2018, 97, 399–404.

(47) Musawwir, A.; Farhat, A.; Khedzad, R. A.; Bhatti, I. A.; Iqbal, J. Theoretical and computational study on electronic effect caused by electron withdrawing/electron-donating groups upon the coumarin thiourea derivatives. *Comput. Theor. Chem.* 2021, 20121, 113271.

(48) Padmanabhan, J.; Parthasarathi, R.; Subramanian, V.; Chattaraj, P. K. Electrophilicity-based charge transfer descriptor. *J. Phys. Chem. A* 2007, 111, 1358–1361.

(49) Vaziri, R.; Vaziri, K.; Bener, E. J.; Bickelhaupt, F. M. Voronoi deformation density (VDD) charges: Assessment of the Mulliken, Bader, Hirshfeld, Weinhold, and VDD Methods for charge analysis. *J. Comput. Chem.* 2004, 25, 189–210.

(50) Bickelhaupt, F. M.; Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Petersson, G.; Nakatsuji, H.; Gaussian 16, Gaussian, Inc.: Wallingford, CT, 2016.

(51) Dennington, R.; Keith, T.; Millam, J. Gaussian 5.0. Gaussian, Inc.: Wallingford, 2008.

(52) Civalleri, B.; Zicovich-Wilson, C. M.; Valenzano, L.; Ugliengo, P. B3LYP augmented with an empirical dispersion term (B3LYP-D) as applied to molecular crystals. *CrystEngComm* 2008, 10, 405–410.

(53) Yanai, T.; Tew, D. P.; Handy, N. C. A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* 2004, 393, 51–57.

(54) Zhang, Y.; Wu, A.; Xu, X.; Yan, Y. OPBE: A promising density functional for the calculation of nuclear shielding constants. *Chem. Phys. Lett.* 2006, 421, 383–388.

(55) Adamo, C.; Barone, V. Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The mPW and mPW1PW models. *J. Chem. Phys.* 1998, 108, 664–675.

(56) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys. Chem. Phys.* 2008, 10, 6615–6620.

(57) Cossi, M.; Barone, V.; Mennucci, B.; Tossi, J. Ab initio study of ionic solutions by a polarizable continuum dielectric model. *Chem. Phys. Lett.* 1998, 286, 253–260.

(58) Ghorelsy, S. SWizard program; University of Ottawa: Ottawa, Canada, 2010.

(59) Li, R.; Fan, W.; Tian, G.; Zhu, H.; He, L.; Cai, J.; Huang, Q.; Cai, Q.; Li, B.; Bai, Y.; Zhang, Z.; Yang, Z.; Xuan, Z.; Ryder, O. A.; Leung, F. C.; Zhou, Y.; Cao, J.; Sun, X.; Fu, Y.; Fang, X.; Guo, X.; Wang, B.; Hou, R.; Shen, F.; Mu, B.; Ni, P.; Lin, R.; Qian, W.; Wang, G.; Yu, C.; Nie, W.; Wang, J.; Wu, Z.; Liang, H.; Min, J.; Wu, Q.; Cheng, S.; Ruan, J.; Wang, M.; Shi, Z.; Zou, W.; Liu, B.; Ren, X.; Zheng, H.; Dong, D.; Cook, K.; Shan, G.; Zhang, H.; Kosiol, C.; Xie, X.; Lu, Z.; Zheng, H.; Li, Y.; Steiner, C. C.; Lam, T.; Lin, S.; Zhang, Q.; Li, G.; Tian, J.; Gong, T.; Liu, H.; Zhang, D.; Fang, L.; Ye, C.; Zhang, J.; Hu, W.; Xu, A.; Ren, Y.; Zhang, G.; Bruford, M. W.; Li, Q.; Ma, L.; Guo, Y.; An, N.; Hu, Y.; Zheng, Y.;
Shi, Y.; Li, Z.; Liu, Q.; Chen, Y.; Zhao, J.; Qu, N.; Zhao, S.; Tian, F.;
Wang, X.; Wang, H.; Xu, L.; Liu, X.; Vinar, T.; Wang, Y.; Lam, T. W.;
Yiu, S. M.; Liu, S.; Zhang, H.; Li, D.; Huang, Y.; Wang, X.; Yang, G.;
Jiang, Z.; Wang, J.; Qin, N.; Li, L.; Li, J.; Bolund, L.; Kristiansen, K.;
Wong, G. K.; Olson, M.; Zhang, X.; Li, S.; Yang, H.; Wang, J.; Wang, J.
The sequence and de novo assembly of the giant panda genome.
Nature 2010, 463, 311–317.
(70) Lu, T.; Chen, F. Multiwfn: a multifunctional wavefunction analyzer.
J. Comput. Chem. 2012, 33, 580–592.