Dear Editor,

We are pleased to submit our manuscript “Theoretical approach towards rational design and characterization of benzo[1,2-b:5-B’]dithiophene (BDT)–based (A-D-A) small molecules of relevance for high performance solar cells ” for publication in the Journal of Material Sciences & Engineering.

Recently, organic materials, including conjugated polymers, organic small molecules and self-assembling organic semiconductors, have intrigued an increasing attention because of their potential to enable the fabrication of flexible, light weight, semi transparency and large-area devices. Among several designed SMs for solution processed solar cells, those including benzo[1,2-b:5-B’]dithiophene (BDT) have been emerging as an attractive building block for donor molecules in OPVs. In this context, a PCE of 9.2% was recently achieved in an OPV device based on BDTT-S-TR/$PC_{70}BM$. In this paper, a series of BDT–based small molecules with acceptor-donor-acceptor (A-D-A) structure were designed based on the experimental system BDTT-S-TR (**1**) for use as potential donor materials for organic photovoltaic (OPV) devices. Their geometry structures, electronic, optical and photovoltaic properties have been investigated by means of density functional theory (DFT) and time dependent density functional theory (TDDFT) methods. The purpose was double; to optimize the energy levels with those of $PC_{70}BM$ and to increase the performance in OPV devices. From this regard, we have predicted the PCEs of the OPVs based on **1-4/$PC_{70}$BM** using Marks model and the results show significant improvement in PCEs compared to the reported system **1/$PC_{70}$BM**. The charge transfer dynamics, including intermolecular charge transfer (inter-CT) and recombination (inter-CR) rates, in **1-4/$PC_{70}$BM** heterojunctions have been examined. The calculations show that the ratio $k_{inter-CT} / k_{inter-CR}$ for the **3/$PC_{70}$BM** and **4/$PC_{70}$BM** heterojunction is **~** $10^4$ times higher than that of the **1/$PC_{70}$BM**.

Consequently, we have identified two new promising photovoltaic donor material (**3** and **4**) for high-efficiency SMs OPVs materials and we hope that this computational study may stimulate experimentalists to synthesize and study these new small molecules; structural parameters, optical and photovoltaic properties were computed, which will facilitate future experimental work.

The manuscript is original and no part of it has been published before, nor is any part of under consideration for publication at another journal.

Yours sincerely,

The authors

# Electronic Supplementary Information (ESI)

## Theoretical approach towards rational design and characterization of benzo[1,2-b:5-B']dithiophene (BDT)–based (A-D-A) small molecules of relevance for high performance solar cells

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| | B3LYP | PBE0 | B3PW91 | Exp in ref [14] |
|---|---|---|---|---|
| HOMO (eV) | -5.03 | -5.20 | -5.16 | -5.18 |

**Table S1.** The HOMO energy (eV) of **1** calculated by different functionals B3LYP, B3PW91 and PBE0 with 6-31G(d) basis set compared with the experimental data.

| | B3PW91 | M06 | M062X | CAM-B3LYP | WB97X(D) | BHandHLYP | Exp in ref [14] |
|---|---|---|---|---|---|---|---|
| $\lambda_{S_0-S_1}$ **(nm)** | 687 | 639 | 523 | 522 | **504** | 538 | 506 |
| $E_{S_0-S_1}$ **(eV)** | 1.80 | 1.94 | 2.37 | 2.37 | **2.46** | 2.30 | 2.45 |

**Table S2.** The first singlet excitation energies ( $E_{S_0-S_1}$ (eV)) and the corresponding absorption wavelength ( $\lambda_{S_0-S_1}$ (nm)) calculated by different functionals with the 6-31G(d) basis set based on the optimized geometry in vacuum at B3PW91/6-31G(d). The calculated values are compared with the experimental data taken from ref 14.

| | PBE0 | M06 | M062X | CAM-B3LYP | WB97X(D) | BHandHLYP | Exp in ref [14] |
|---|---|---|---|---|---|---|---|
| $\lambda_{S_0-S_1}$ **(nm)** | 638 | 632 | 517 | 516 | **498** | 531 | 506 |
| $E_{S_0-S_1}$ **(eV)** | 1.94 | 1.96 | 2.40 | 2.40 | **2.49** | 2.33 | 2.45 |

**Table S3.** The first singlet excitation energies ( $E_{S_0-S_1}$ (eV)) and the corresponding absorption wavelength ( $\lambda_{S_0-S_1}$ (nm) calculated by different functionals with the 6-31G(d) basis set based on the optimized geometry in vacuum at PBE0/6-31G(d). The calculated values are compared with the experimental data taken from ref 14.

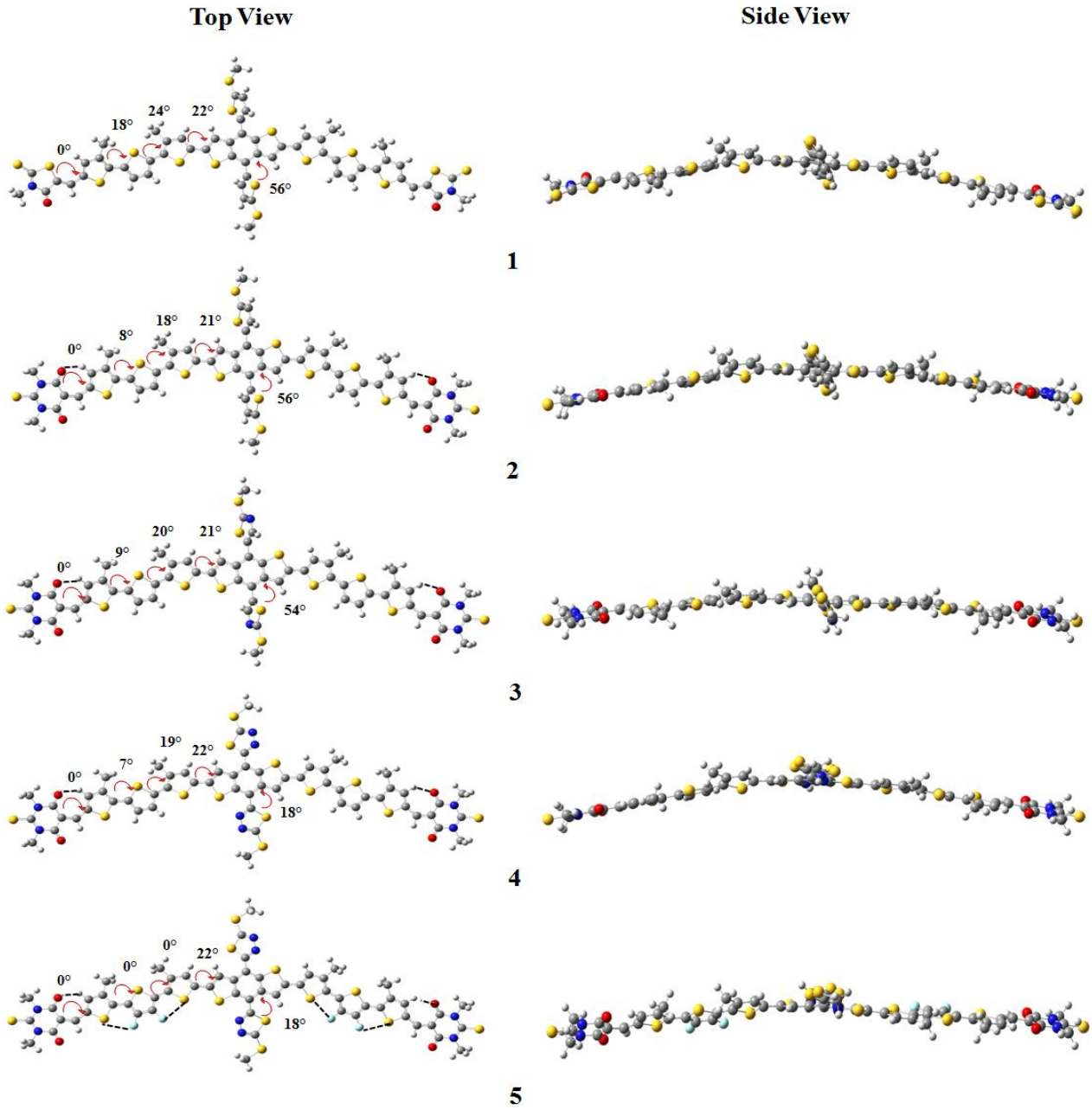


**Figure S1.** Optimized geometries of SMs **1-5** at the B3PW91/6-31G(d) level of theory with the dihedral angles between donor and acceptor units.

| | 1/$PC_{70}BM$ | | |
|---|---|---|---|
| | **E/eV (λ/nm)** | **f** | **Excited-state property** |
| **$S_1$** | 2.33 (532) | 0.0023 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_2$** | 2.48 (499) | 0.0138 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_3$** | 2.49 (497) | 4.6336 | Local excited (LE) transition on 1 |
| **$S_4$** | 2.60 (477) | 0.0355 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_5$** | 2.65 (468) | 0.0160 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_6$** | 2.70 (458) | 0.2175 | Local excited (LE) transition on 1 |
| **$S_7$** | 2.77 (446) | 0.0305 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_8$** | 2.83 (437) | 0.0030 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_9$** | 2.85 (433) | 0.0051 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{10}$** | 2.86 (433) | 0.0086 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{11}$** | 2.88 (429) | 0.0049 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{12}$** | 2.91 (425) | 0.0073 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{13}$** | 2.96 (419) | 0.0005 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{14}$** | 3.00 (413) | 0.0024 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{15}$** | 3.02 (410) | 0.0003 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{16}$** | 3.04 (407) | 0.0000 | Intermolecular charge transfer (inter-CT) |
| **$S_{17}$** | 3.05 (406) | 0.0002 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{18}$** | 3.09 (400) | 0.0014 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{19}$** | 3.10 (400) | 0.0015 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{20}$** | 3.12 (398) | 0.0163 | Local excited (LE) transition on $PC_{70}BM$ |

**Table S4.** Calculated electronic transition energies (eV) and corresponding excitation oscillator strengths (f) for **1/$PC_{70}BM$** heterojunction at TDDFT/CAM-B3LYP/6-31G(d).

| | 2/$PC_{70}BM$ | | |
|---|---|---|---|
| | **E/eV (λ/nm)** | **f** | **Excited-state property** |
| **$S_1$** | 2.32 (533) | 0.0031 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_2$** | 2.42 (512) | 4.3257 | Local excited (LE) transition on 2 |
| **$S_3$** | 2.48 (500) | 0.0614 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_4$** | 2.59 (478) | 0.1014 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_5$** | 2.63 (470) | 0.5767 | Local excited (LE) transition on 2 |
| **$S_6$** | 2.65 (468) | 0.0049 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_7$** | 2.77 (448) | 0.0295 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_8$** | 2.83 (438) | 0.0024 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_9$** | 2.85 (434) | 0.0046 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{10}$** | 2.86 (433) | 0.0099 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{11}$** | 2.87 (432) | 0.0013 | Pure Intermolecular charge transfer |
| **$S_{12}$** | 2.88 (431) | 0.0024 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{13}$** | 2.91 (426) | 0.0086 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{14}$** | 2.96 (419) | 0.0006 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{15}$** | 3.00 (413) | 0.0017 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{16}$** | 3.02 (410) | 0.0003 | Pure Intermolecular charge transfer |
| **$S_{17}$** | 3.05 (405) | 0.0001 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{18}$** | 3.08 (401) | 0.0002 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{19}$** | 3.09 (401) | 0.0017 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{20}$** | 3.10 (400) | 0.0011 | Local excited (LE) transition on $PC_{70}BM$ |

**Table S5.** Calculated electronic transition energies (eV) and corresponding excitation oscillator strengths (f) for **2/$PC_{70}BM$** heterojunction at TDDFT/CAM-B3LYP/6-31G(d).

| | 3/$PC_{70}BM$ | | |
|---|---|---|---|
| | **E/eV (λ/nm)** | **f** | **Excited-state property** |
| **$S_1$** | 2.33 (532) | 0.0020 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_2$** | 2.44 (508) | 4.5200 | Local excited (LE) transition on 3 |
| **$S_3$** | 2.47 (502) | 0.0759 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_4$** | 2.60 (477) | 0.0842 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_5$** | 2.64 (470) | 0.3286 | Local excited (LE) transition on 3 |
| **$S_6$** | 2.65 (467) | 0.0187 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_7$** | 2.77 (448) | 0.0285 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_8$** | 2.83 (438) | 0.0019 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_9$** | 2.85 (435) | 0.0069 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{10}$** | 2.86 (433) | 0.0023 | Intermolecular charge transfer (inter-CT) |
| **$S_{11}$** | 2.87 (433) | 0.0096 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{12}$** | 2.88 (430) | 0.0053 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{13}$** | 2.91 (425) | 0.0054 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{14}$** | 2.96 (418) | 0.0005 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{15}$** | 3.00 (413) | 0.0022 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{16}$** | 3.01 (411) | 0.0003 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{17}$** | 3.06 (404) | 0.0003 | Intermolecular charge transfer (inter-CT) |
| **$S_{18}$** | 3.07 (403) | 0.0002 | Intermolecular charge transfer (inter-CT) |
| **$S_{19}$** | 3.10 (400) | 0.0007 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{20}$** | 3.10 (400) | 0.0034 | Local excited (LE) transition on $PC_{70}BM$ |

**Table S6.** Calculated electronic transition energies (eV) and corresponding excitation oscillator strengths (f) for **3/$PC_{70}BM$** heterojunction at TDDFT/CAM-B3LYP/6-31G(d).

| | 4/$PC_{70}BM$ | | |
|---|---|---|---|
| | **E/eV (λ/nm)** | **f** | **Excited-state property** |
| **$S_1$** | 2.33 (532) | 0.0015 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_2$** | 2.39 (518) | 4.3839 | Local excited (LE) transition on 4 |
| **$S_3$** | 2.47 (502) | 0.0507 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_4$** | 2.56 (477) | 0.1359 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_5$** | 2.62 (473) | 0.2554 | Local excited (LE) transition on 4 |
| **$S_6$** | 2.65 (467) | 0.0191 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_7$** | 2.77 (448) | 0.0331 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_8$** | 2.83 (438) | 0.0025 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_9$** | 2.85 (435) | 0.0058 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{10}$** | 2.86 (432) | 0.0130 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{11}$** | 2.87 (431) | 0.0003 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{12}$** | 2.90 (427) | 0.0102 | Intermolecular charge transfer (inter-CT) |
| **$S_{13}$** | 2.94 (421) | 0.0008 | Intermolecular charge transfer (inter-CT) |
| **$S_{14}$** | 2.96 (419) | 0.0032 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{15}$** | 2.98 (415) | 0.3687 | Local excited (LE) transition on 4 |
| **$S_{16}$** | 3.00 (413) | 0.0027 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{17}$** | 3.01 (411) | 0.0016 | Intermolecular charge transfer (inter-CT) |
| **$S_{18}$** | 3.06 (404) | 0.0001 | Intermolecular charge transfer (inter-CT) |
| **$S_{19}$** | 3.09 (400) | 0.0010 | Local excited (LE) transition on $PC_{70}BM$ |
| **$S_{20}$** | 3.10 (400) | 0.0045 | Local excited (LE) transition on $PC_{70}BM$ |

**Table S7.** Calculated electronic transition energies (eV) and corresponding excitation oscillator strengths (f) for **4/$PC_{70}BM$** heterojunction at TDDFT/CAM-B3LYP/6-31G(d).