**Effect of number and position of methoxy substituents on fine tuning the electronic structures and photophysical properties of designed carbazole-based hole-transporting materials for perovskite solar cells: DFT calculations**

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**Supplementary data**

**DFT Details and equations**

DFT and TD-DFT methods were used to investigate the structural, electronic and optical properties of the studied compounds. The more computationally efficient B3LYP density functional Becke-three–Lee–Yang–Parr (B3LYP) (Becke 1988, Lee, Yang et al. 1988) was selected for optimization of the ground state (S0) and excited state (S1) geometries of all compounds. The functional has been proved as a suitable method for predicting such geometries/properties (Chen, Jia et al. 2014, Bagheri Novir and Hashemianzadeh 2015, Chi and Li 2015). The standard 6-31G(d) basis set was used for the optimizations. The use of a 6-31G(d) split-valence double zeta basis set without diffuse functions prevents convergence difficulties in delocalized systems, yet leads to accurate geometries at a reasonable computational cost (Pogantsch, Heimel et al. 2002, Gao 2010).

The parent hole transporting material (R01) and its twelve designed derivatives (D1 to H12) geometries were optimized with C1 point group. The optimized geometries show no imaginary frequencies, which ensure energetic minima. The total electronic energies of neutral, cationic, and anionic forms of these compounds were used to compute the reorganization energy (), the adiabatic () and vertical ionization potential), the adiabatic () and vertical electron affinity (), the hole extraction potential and the electron extraction potential at the same level of DFT method, according to the following equations: (Chi and Li 2015)

|  |  |
| --- | --- |
|  | Equation 1 |
|  | Equation 2 |
|  | Equation 3 |
| ; | Equation 4 |
| ; | Equation 5 |
| ; | Equation 6 |

Where, is the energy of cation/anion with neutral structure,  is the energy of cation/anion with cationic/anionic structure, is the energy of neutral structure at cationic/anionic state, is the energy of neutral structure. The light harvesting efficiency (LHE), given by:

|  |  |
| --- | --- |
|  | Equation 7 |

where is the oscillator strength at the *.* The exciton binding energy of these compounds () was defined as the potential energy difference between the neutral singlet exciton and free charge carriers and was calculated according to the following equation:

|  |  |
| --- | --- |
|  | Equation 8 |

where is the electronic band gap and can be replaced by the energy gap, and is the optical gap and is defined as the first singlet excitation energy(Chi and Li 2015).

The absorption and emission spectra were determined on the optimized S0 and S1 geometries, respectively, using TD-B3LYP/6-311++G(d,p) level. The radiative lifetime was calculated using Einstein transition probabilities according to the following equation (Hilborn 1982):

|  |  |
| --- | --- |
|  | Equation 9 |

Where is the speed of light (in a.u. c = 137.036),is the fluorescent energy and is the oscillator strength (in a.u. unit). Note that, 1 au of time = 2.419 x 10-17 sec. The absolute hardness was calculated using the adiabatic ionization potential and electron affinity according to the following equation:

|  |  |
| --- | --- |
|  | Equation 10 |

The rate constant for charge transfer, , can be expressed in Equation 11. The rate constant for charge transfer, , for hole and electron can be calculated based on the Marcus Hush electron-transfer theory, (Marcus 1993) which is given by the following equation:

|  |  |
| --- | --- |
|  | Equation 11 |

where *is* the reorganization energy for hole or electro,T is the absolute temperature, *h* and *kB* are the Planck and Boltzmann constants respectively and is the charge transfer integral (electronic coupling) and is given bythe following equations.This approximation has been proved to be reasonable for organic solids in weak polar media, the details of the validity of Equation 11can be found in relevant literature (Bromley, Mas-Torrent et al. 2004, Norton and Brédas 2008).

On the other hand, the charge transfer integral () describes the overlap of the electronic wave functions between the donor and acceptor states, which intensively depends on the relative molecular arrangement in the solid state (Mohakud, Alex et al. 2010). Currently, the value can be calculated mainly by three methods: (1) the site-energy corrected method (Valeev, Coropceanu et al. 2006), (2) the direct coupling method (Lin, Cheng et al. 2005) and (3) the Koopmans’s theorem approximation method (Bendikov, Wudl et al. 2004, Yang, Li et al. 2007). Here, we only outline the approach used in this work, the Koopmans’s theorem approximation method, which has been extensively used to estimate the t value in organic crystals (Cornil, Lemaur et al. 2002, Lemaur, da Silva Filho et al. 2004). According to this method, the t can be calculated with the splitting of HOMO (LUMO) and HOMO-1 (LUMO+1) energies in dimers for the hole (electron) transfer (Datta, Mohakud et al. 2007):

|  |  |
| --- | --- |
| ; | Equation 12 |

where , , , and are the energies of the HOMO, HOMO-1, LUMO+1, and LUMO taken from the neutral monomer. It should be noticed that when the dimer is not co-facially stacked, the correction of site energy is essential (Datta, Mohakud et al. 2007).

The polarizability, total hyperpolarizability, and total hyperpolarizability values were computed as numerical derivatives of dipole moments at the B3LYP/6-311++G(d,p), related equations can be found in relevant literature (Garza, Wazzan et al. 2014).

Table SD 1: Bond distances (in Å), bond angles, and torsional angles (in o) of the ground state (So) of designed tetra-methoxy derivatives (T8-T11) in their neutral, cationic and anionic forms, data in parenthesis belong to the first excited state (S1)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **T8** |  | S−C5 | C5−C28 | S−C5−C28−C29 | C30−O73 | C30−O73−C78 |
| neutral | 1.7565  (1.8009) | 1.4700  (1.4238) | 46.925  (25.172) | 1.3809  (1.3781) | 113.673  (113.719) |
| cationic | 1.7561 | 1.4682 | 45.592 | 1.3647 | 115.541 |
| anionic | 1.7836 | 1.4402 | 28.543 | 1.3869 | 113.231 |
| **T9** |  | S−C5 | C5−C28 | S−C5−C28−C29 | C30−O69 | C30−O69−C78 |
| neutral | 1.7572  (1.8057) | 1.4738  (1.4401) | 58.003  (43.681) | 1.3818  (1.3802) | 114.042  (113.933) |
| cationic | 1.7603 | 1.4485 | 42.209 | 1.3514 | 118.977 |
| anionic | 1.7824 | 1.4490 | 43.884 | 1.3879 | 113.770 |
| **T10** |  | S−C5 | C5−C28 | S−C5−C28−C29 | C29−O69 | C29−O69−C78 |
| neutral | 1.7591  (1.8039) | 1.4700  (1.4178) | 32.982  (16.612) | 1.3879  (1.3841) | 114.045  (113.910) |
| cationic | 1.7661 | 1.4447 | 19.573 | 1.3756 | 114.670 |
| anionic | 1.7869 | 1.4377 | 21.112 | 1.3962 | 113.070 |
| **T11** |  | S−C5 | C5−C27 | S−C5−C27−C28 | C29−O65 | C29−O69−C66 |
| neutral | 1.7575  (1.8005) | 1.4700  (1.4230) | 47.192  (22.728) | 1.3815  (1.3763) | 114.098  (114.959) |
| cationic | 1.7572 | 1.4540 | 38.208 | 1.3478 | 119.404 |
| anionic | 1.7829 | 1.4421 | 28.236 | 1.3871 | 114.404 |

Table SD 2: Bond distances (in Å), bond angles, and torsional angles (in o) of the ground state of designed hexa-methoxy derivative (H12) in its neutral, cationic and anionic forms, the data in parenthesis belong to the first excited state.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **H12** |  | S−C5 | C5−C28 | S−C5−C28−C29 | C29−O74 | C29−O74−C84 |
| neutral | 1.7562  (1.8021) | 1.4735  (1.4397) | 56.204  (45.493) | 1.3800  (1.3798) | 113.810  (115.771) |
| cationic | 1.7621 | 1.4497 | 42.171 | 1.3739 | 114.226 |
| anionic | 1.7830 | 1.4473 | 42.990 | 1.3870 | 112.817 |

**Table SD 3: Isotropic polarizabilities and polarizabilities anisotropic along with their individual tensor components (in au) of investigated HTMs calculated at the B3LYP/6-311++G(d,p)**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| HTM |  |  |  |  |  |  |  |  |
| R01 | 840 | -1 | 446 | -38 | 7 | 195 | 494 | 568 |
| D1 | 857 | -1 | 464 | 1 | 38 | 224 | 501 | 557 |
| D2 | 776 | -5 | 399 | -31 | 1 | 329 | 515 | 420 |
| D3 | 866 | -1 | 494 | -23 | 7 | 221 | 456 | 562 |
| D4 | 817 | -2 | 451 | -30 | 4 | 272 | 513 | 484 |
| D5 | 949 | -1 | 467 | -29 | 6 | 217 | 544 | 647 |
| D6 | 854 | -7 | 430 | -32 | 0 | 270 | 518 | 525 |
| D7 | 856 | 11 | 429 | -31 | -10 | 271 | 519 | 528 |
| T8 | 798 | -4 | 424 | -12 | 1 | 354 | 525 | 414 |
| T9 | 781 | -8 | 372 | -39 | 3 | 389 | 514 | 406 |
| T10 | 883 | 0 | 501 | -41 | 6 | 266 | 550 | 543 |
| T11 | 875 | -4 | 406 | -20 | 1 | 351 | 544 | 500 |
| H12 | 809 | -8 | 419 | -26 | 2 | 410 | 546 | 397 |

Table SD 4: Total hyperpolarizabilities along with their individual tensor components (in au) of investigated HTMs calculated at the B3LYP/6-311++G(d,p)

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| HTM |  |  |  |  |  |  |  |  |  |  |  |
| R01 | 5 | -619 | 11 | -91 | -49 | 73 | -2 | 3 | 10 | 17 | 700 |
| D1 | 20 | -583 | -11 | -66 | 275 | -11 | 36 | 7 | 5 | -151 | 644 |
| D2 | -31 | -1142 | 35 | -145 | -5 | 95 | -12 | -5 | -37 | 34 | 1291 |
| D3 | 30 | 168 | 3 | -19 | -13 | 156 | 1 | 4 | 20 | 19 | 174 |
| D4 | -977 | -615 | -195 | -68 | -109 | 133 | 19 | -39 | -18 | -5 | 1399 |
| D5 | 13 | -784 | 9 | -31 | -58 | 159 | 2 | 3 | -23 | 13 | 1420 |
| D6 | 120 | -746 | 121 | -131 | -4 | 179 | 47 | 62 | 9 | 35 | 919 |
| D7 | -19 | -762 | -71 | -109 | 201 | 180 | 20 | 3 | 9 | 48 | 866 |
| T8 | -10 | -567 | 31 | -4 | -12 | 221 | -13 | -15 | -16 | 26 | 587 |
| T9 | -86 | -165 | 28 | -91 | -16 | 96 | 0 | -7 | 8 | 21 | 256 |
| T10 | -30 | 31 | -5 | -41 | -41 | 111 | 4 | 5 | -1 | 13 | 32 |
| T11 | -26 | -805 | 40 | -182 | -13 | 257 | -10 | -22 | 29 | 29 | 959 |
| H12 | -54 | -119 | 36 | 31 | -33 | 144 | -5 | -13 | -3 | 30 | 96 |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | HOMO | LUMO |  | HOMO | LUMO |
| R01 |  |  | T8 |  |  |
| D5 |  |  | H12 |  |  |
| T11 |  |  |  |  |  |

Figure SD 1: HOMO and LUMO orbitals distribution for the first excited state (S1) of the investigated HTMs

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