# Exploring organic semiconductors in solution: The effects of solvation, alkylization, and doping Supplementary Material

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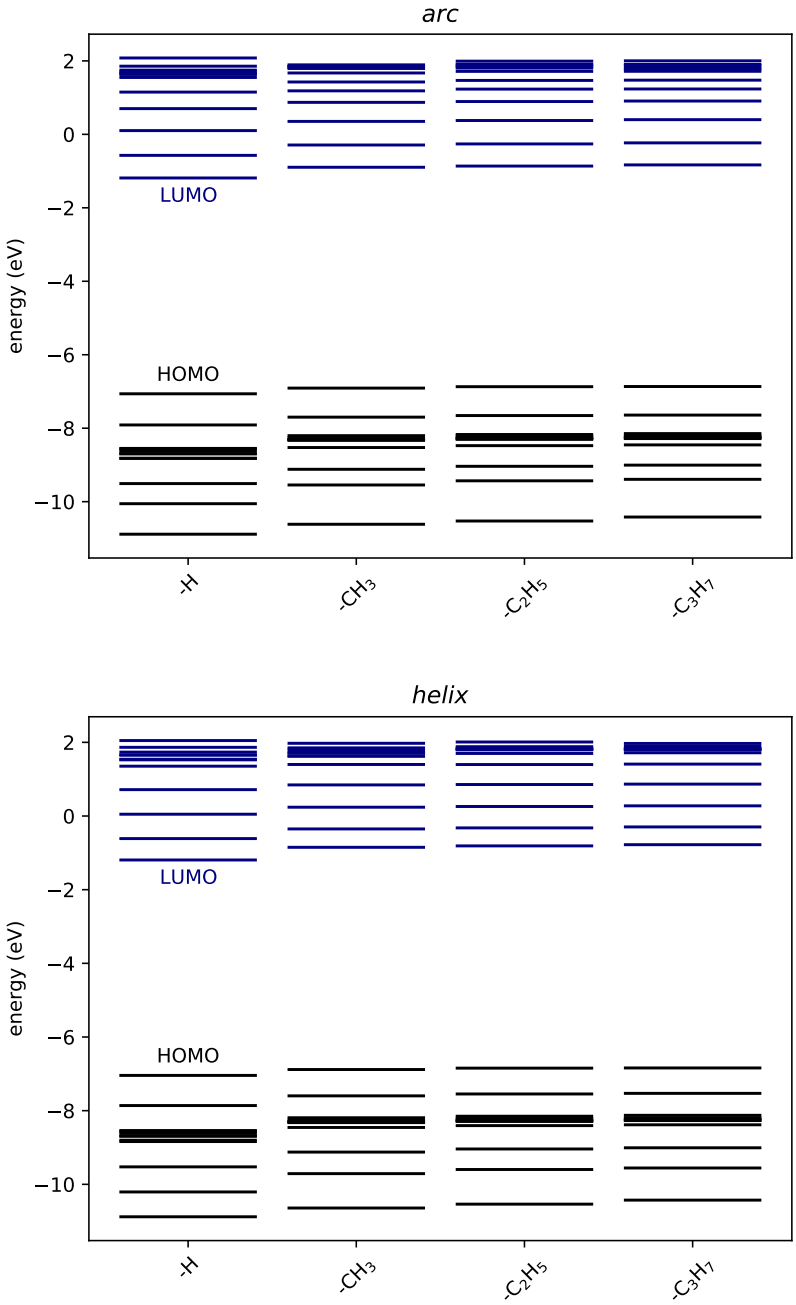
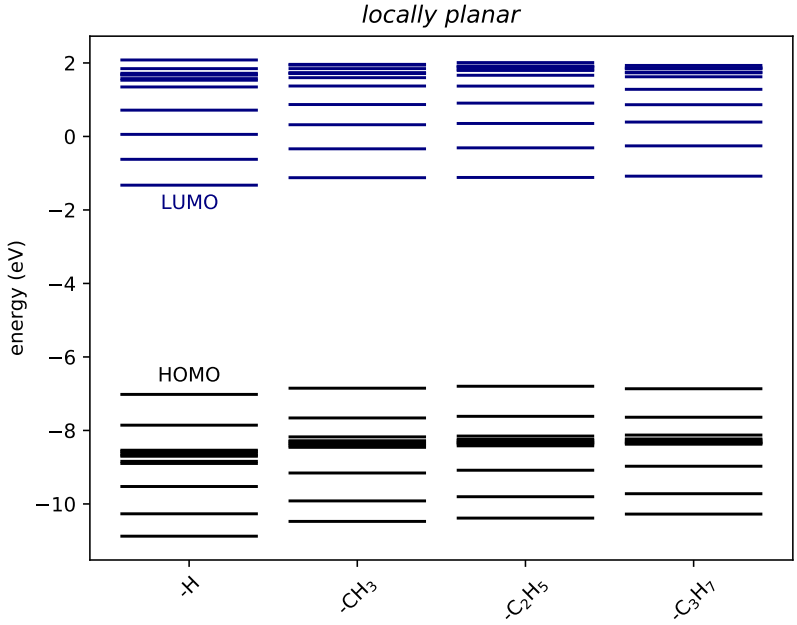
February 11, 2021

## Contents

## S1 Energy levels in 6T, different alkyl groups (*in vacuo*)

12 highest occupied and 12 lowest virtual orbitals






## S2 Charge transfer in 6T/F4-TCNQ: Values

(the *in vacuo* rows correspond to a calculation using the geometry of the respective solvated system, but not taking into account solvation effects directly)

| solvent → | none | $C_6H_6$ | $CHCl_3$ | $CH_3NO_2$ |
|---|---|---|---|---|
| $\varepsilon$ | 1.00 | 2.27 | 4.71 | 36.5 |
| $2(\varepsilon\text{-}1)/(2\varepsilon\text{+}1)$ | 0.00 | 0.46 | 0.71 | 0.96 |
| CT (-H) | 0.277 | 0.317 | 0.338 | 0.357 |
| CT (-H, *in vacuo*) | 0.277 | 0.282 | 0.284 | 0.285 |
| CT (-$CH_3$) | 0.387 | 0.448 | 0.482 | 0.520 |
| CT (-$CH_3$, *in vacuo*) | 0.387 | 0.405 | 0.412 | 0.416 |
| CT (-$C_2H_5$) | 0.441 | | | |
| CT (-$C_3H_7$) | 0.450 | | | |

## S3 Excitations from LR-TDDFT: 6T alone

(all single-particle transitions with weight ≥10% listed)

### S3.1 *in vacuo*, different alkyl groups, cc-pVDZ

#### S3.1.1 *arc*

**-H**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.11 | 2.03 | H→L (87%) |
| 2 | 3.79 | 0.02 | H→L+1 (51%)<br>H-1→L (40%) |
| 3 | 4.39 | 0.14 | H→L+2 (41%)<br>H-1→L+1 (31%)<br>H-2→L (17%) |
| 4 | 4.44 | 0.00 | H-1→L (48%)<br>H→L+1 (35%) |
| 5 | 4.85 | 0.00 | H→L+3 (38%)<br>H-1→L+2 (21%)<br>H-7→L (12%)<br>H-2→L+1 (11%) |

**-$CH_3$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.22 | 1.91 | H→L (86%) |
| 2 | 3.88 | 0.05 | H→L+1 (51%)<br>H-1→L (39%) |
| 3 | 4.44 | 0.13 | H→L+2 (41%)<br>H-1→L+1 (30%)<br>H-2→L (17%) |
| 4 | 4.54 | 0.00 | H-1→L (46%)<br>H→L+1 (34%) |
| 5 | 4.86 | 0.01 | H→L+3 (43%)<br>H-1→L+2 (19%) |

**-$C_2H_5$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.21 | 1.90 | H→L (86%) |
| 2 | 3.86 | 0.06 | H→L+1 (51%)<br>H-1→L (39%) |
| 3 | 4.42 | 0.12 | H→L+2 (42%)<br>H-1→L+1 (30%)<br>H-2→L (17%) |
| 4 | 4.53 | 0.00 | H-1→L (46%)<br>H→L+1 (33%) |
| 5 | 4.85 | 0.01 | H→L+3 (42%)<br>H-1→L+2 (20%) |

**-$C_3H_7$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.23 | 1.88 | H→L (86%) |
| 2 | 3.87 | 0.07 | H→L+1 (51%)<br>H-1→L (39%) |
| 3 | 4.44 | 0.13 | H→L+2 (41%)<br>H-1→L+1 (30%)<br>H-2→L (17%) |
| 4 | 4.55 | 0.00 | H-1→L (46%)<br>H→L+1 (33%) |
| 5 | 4.86 | 0.01 | H→L+3 (42%)<br>H-1→L+2 (20%) |

### S3.1.2 *helix*

**-H**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.10 | 1.99 | H→L (86%) |
| 2 | 3.76 | 0.00 | H→L+1 (51%)<br>H-1→L (40%) |
| 3 | 4.34 | 0.16 | H→L+2 (38%)<br>H-1→L+1 (34%)<br>H-2→L (18%) |
| 4 | 4.39 | 0.00 | H-1→L (47%)<br>H→L+1 (35%) |
| 5 | 4.85 | 0.00 | H→L+3 (27%)<br>H-1→L+2 (25%)<br>H-2→L+1 (17%)<br>H-6→L (12%) |

**-$CH_3$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.29 | 1.87 | H→L (85%) |
| 2 | 3.87 | 0.00 | H→L+1 (51%)<br>H-1→L (39%) |
| 3 | 4.38 | 0.16 | H→L+2 (37%)<br>H-1→L+1 (35%)<br>H-2→L (18%) |
| 4 | 4.49 | 0.00 | H-1→L (45%)<br>H→L+1 (32%) |
| 5 | 4.85 | 0.01 | H→L+3 (28%)<br>H-1→L+2 (27%)<br>H-2→L+1 (18%) |

**-$C_2H_5$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.29 | 1.84 | H→L (85%) |
| 2 | 3.86 | 0.00 | H→L+1 (51%)<br>H-1→L (39%) |
| 3 | 4.36 | 0.16 | H→L+2 (37%)<br>H-1→L+1 (35%)<br>H-2→L (18%) |
| 4 | 4.48 | 0.00 | H-1→L (45%)<br>H→L+1 (32%) |
| 5 | 4.83 | 0.02 | H-1→L+2 (28%)<br>H→L+3 (28%)<br>H-2→L+1 (19%) |

**-$C_3H_7$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.31 | 1.82 | H→L (85%) |
| 2 | 3.87 | 0.01 | H→L+1 (51%)<br>H-1→L (39%) |
| 3 | 4.37 | 0.17 | H→L+2 (36%)<br>H-1→L+1 (35%)<br>H-2→L (18%) |
| 4 | 4.50 | 0.00 | H-1→L (45%)<br>H→L+1 (32%) |
| 5 | 4.83 | 0.02 | H-1→L+2 (28%)<br>H→L+3 (28%)<br>H-2→L+1 (19%) |

#### S3.1.3 *locally planar*

**-H**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 2.87 | 1.97 | H→L (89%) |
| 2 | 3.66 | 0.01 | H→L+1 (54%)<br>H-1→L (37%) |
| 3 | 4.20 | 0.00 | H-1→L (51%)<br>H→L+1 (34%) |
| 4 | 4.27 | 0.18 | H→L+2 (42%)<br>H-1→L+1 (31%)<br>H-2→L (16%) |
| 5 | 4.78 | 0.01 | H-2→L (47%)<br>H→L+2 (33%) |

**-$CH_3$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 2.81 | 1.92 | H→L (91%) |
| 2 | 3.67 | 0.01 | H→L+1 (58%) |
| | | | H-1→L (33%) |
| 3 | 4.16 | 0.02 | H-1→L (55%) |
| | | | H→L+1 (29%) |
| 4 | 4.30 | 0.19 | H→L+2 (49%) |
| | | | H-1→L+1 (27%) |
| | | | H-2→L (11%) |
| 5 | 4.72 | 0.01 | H-2→L (26%) |
| | | | H→L+3 (20%) |
| | | | H→L+2 (13%) |

**-$C_2H_5$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 2.74 | 1.93 | H→L (91%) |
| 2 | 3.62 | 0.00 | H→L+1 (59%) |
| | | | H-1→L (32%) |
| 3 | 4.10 | 0.02 | H-1→L (56%) |
| | | | H→L+1 (28%) |
| 4 | 4.26 | 0.19 | H→L+2 (49%) |
| | | | H-1→L+1 (26%) |
| | | | H-2→L (11%) |
| 5 | 4.68 | 0.02 | H-2→L (35%) |
| | | | H→L+3 (15%) |
| | | | H→L+2 (14%) |

**-$C_3H_7$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 2.79 | 1.85 | H→L (91%) |
| 2 | 3.68 | 0.00 | H→L+1 (60%) |
| | | | H-1→L (31%) |
| 3 | 4.17 | 0.03 | H-1→L (56%) |
| | | | H→L+1 (27%) |
| 4 | 4.32 | 0.17 | H→L+2 (45%) |
| | | | H-1→L+1 (26%) |
| | | | H-2→L (12%) |
| 5 | 4.71 | 0.01 | H-2→L (29%) |
| | | | H→L+3 (21%) |

## S3.2 different solvents, $CH_3$-functionalized, cc-pVDZ

### S3.2.1 *arc*

***in vacuo***

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.22 | 1.91 | H→L (86%) |
| 2 | 3.88 | 0.05 | H→L+1 (51%)<br>H-1→L (39%) |
| 3 | 4.44 | 0.13 | H→L+2 (41%)<br>H-1→L+1 (30%)<br>H-2→L (17%) |
| 4 | 4.54 | 0.00 | H-1→L (46%)<br>H→L+1 (34%) |
| 5 | 4.86 | 0.01 | H→L+3 (43%)<br>H-1→L+2 (19%) |

**benzene (apolar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.10 | 2.10 | H→L (86%) |
| 2 | 3.74 | 0.06 | H→L+1 (50%)<br>H-1→L (40%) |
| 3 | 4.34 | 0.17 | H→L+2 (40%)<br>H-1→L+1 (31%)<br>H-2→L (18%) |
| 4 | 4.50 | 0.00 | H-1→L (46%)<br>H→L+1 (35%) |
| 5 | 4.81 | 0.01 | H→L+3 (41%)<br>H-1→L+2 (21%) |

**chloroform (semi-polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.06 | 2.10 | H→L (87%) |
| 2 | 3.72 | 0.05 | H→L+1 (50%)<br>H-1→L (40%) |
| 3 | 4.33 | 0.17 | H→L+2 (40%)<br>H-1→L+1 (31%)<br>H-2→L (18%) |
| 4 | 4.47 | 0.00 | H-1→L (46%)<br>H→L+1 (35%) |
| 5 | 4.80 | 0.01 | H→L+3 (41%)<br>H-1→L+2 (21%) |

**nitromethane (polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.03 | 2.10 | H→L (87%) |
| 2 | 3.70 | 0.04 | H→L+1 (50%)<br>H-1→L (40%) |
| 3 | 4.32 | 0.17 | H→L+2 (40%)<br>H-1→L+1 (31%)<br>H-2→L (18%) |
| 4 | 4.42 | 0.00 | H-1→L (47%)<br>H→L+1 (35%) |
| 5 | 4.80 | 0.01 | H→L+3 (40%)<br>H-1→L+2 (21%) |

### S3.2.2 *helix*

***in vacuo***

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.29 | 1.87 | H→L (85%) |
| 2 | 3.87 | 0.00 | H→L+1 (51%)<br>H-1→L (39%) |
| 3 | 4.38 | 0.16 | H→L+2 (37%)<br>H-1→L+1 (35%)<br>H-2→L (18%) |
| 4 | 4.49 | 0.00 | H-1→L (45%)<br>H→L+1 (32%) |
| 5 | 4.85 | 0.01 | H→L+3 (28%)<br>H-1→L+2 (27%)<br>H-2→L+1 (18%) |

**benzene (apolar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.11 | 2.06 | H→L (86%) |
| 2 | 3.71 | 0.00 | H→L+1 (50%)<br>H-1→L (39%) |
| 3 | 4.28 | 0.21 | H→L+2 (37%)<br>H-1→L+1 (34%)<br>H-2→L (19%) |
| 4 | 4.44 | 0.00 | H-1→L (45%)<br>H→L+1 (34%) |
| 5 | 4.79 | 0.01 | H→L+3 (29%)<br>H-1→L+2 (26%)<br>H-2→L+1 (17%) |

**chloroform (semi-polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 3.07 | 2.07 | H→L (86%) |
| 2 | 3.69 | 0.00 | H→L+1 (51%)<br>H-1→L (39%) |
| 3 | 4.27 | 0.20 | H→L+2 (37%)<br>H-1→L+1 (34%)<br>H-2→L (19%) |
| 4 | 4.41 | 0.00 | H-1→L (46%)<br>H→L+1 (34%) |
| 5 | 4.79 | 0.01 | H→L+3 (29%)<br>H-1→L+2 (26%)<br>H-2→L+1 (16%) |

**nitromethane (polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 2.96 | 2.10 | H→L (87%) |
| 2 | 3.64 | 0.00 | H→L+1 (51%)<br>H-1→L (39%) |
| 3 | 4.25 | 0.20 | H→L+2 (39%)<br>H-1→L+1 (32%)<br>H-2→L (18%) |
| 4 | 4.33 | 0.00 | H-1→L (47%)<br>H→L+1 (34%) |
| 5 | 4.78 | 0.00 | H→L+3 (28%)<br>H-1→L+2 (21%)<br>H-2→L+1 (12%) |

### S3.2.3 *locally planar*

***in vacuo***

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 2.81 | 1.92 | H→L (91%) |
| 2 | 3.67 | 0.01 | H→L+1 (58%)<br>H-1→L (33%) |
| 3 | 4.16 | 0.02 | H-1→L (55%)<br>H→L+1 (29%) |
| 4 | 4.30 | 0.19 | H→L+2 (49%)<br>H-1→L+1 (27%)<br>H-2→L (11%) |
| 5 | 4.72 | 0.01 | H-2→L (26%)<br>H→L+3 (20%)<br>H→L+2 (13%) |

**benzene (apolar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 2.66 | 2.11 | H→L (90%) |
| 2 | 3.50 | 0.01 | H→L+1 (55%)<br>H-1→L (36%) |
| 3 | 4.10 | 0.05 | H-1→L (49%)<br>H→L+1 (30%) |
| 4 | 4.17 | 0.20 | H→L+2 (42%)<br>H-1→L+1 (28%)<br>H-2→L (13%) |
| 5 | 4.67 | 0.01 | H-2→L (28%)<br>H→L+3 (17%)<br>H→L+2 (16%) |

**chloroform (semi-polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 2.66 | 2.11 | H→L (90%) |
| 2 | 3.50 | 0.01 | H→L+1 (55%)<br>H-1→L (36%) |
| 3 | 4.09 | 0.04 | H-1→L (50%)<br>H→L+1 (30%) |
| 4 | 4.16 | 0.21 | H→L+2 (43%)<br>H-1→L+1 (29%)<br>H-2→L (14%) |
| 5 | 4.66 | 0.01 | H-2→L (36%)<br>H→L+2 (20%)<br>H→L+3 (11%) |

**nitromethane (polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 2.66 | 2.10 | H→L (91%) |
| 2 | 3.50 | 0.01 | H→L+1 (55%)<br>H-1→L (36%) |
| 3 | 4.07 | 0.03 | H-1→L (51%)<br>H→L+1 (31%) |
| 4 | 4.15 | 0.21 | H→L+2 (44%)<br>H-1→L+1 (29%)<br>H-2→L (14%) |
| 5 | 4.65 | 0.01 | H-2→L (43%)<br>H→L+2 (25%) |

## S4 Excitations from LR-TDDFT: 6T/F4-TCNQ

(all single-particle transitions with weight ≥10% listed)

### S4.1 *in vacuo*, different alkyl groups, cc-pVDZ

**-H**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.46 | 0.10 | H→L (97%) |
| 2 | 2.03 | 0.32 | H-1→L (95%) |
| 3 | 2.76 | 0.43 | H→L+1 (63%)<br>H-3→L (28%) |
| 4 | 3.01 | 0.02 | H-2→L (85%) |
| 5 | 3.10 | 0.01 | H-9→L (74%)<br>H-12→L (14%) |
| 6 | 3.12 | 2.12 | H-3→L (67%)<br>H→L+1 (26%) |
| 7 | 3.43 | 0.00 | H-10→L (61%)<br>H-6→L (28%) |
| 8 | 3.54 | 0.01 | H-1→L+1 (71%)<br>H→L+2 (19%) |
| 9 | 3.59 | 0.01 | H-7→L (73%)<br>H-5→L (14%) |
| 10 | 3.61 | 0.01 | H-6→L (51%)<br>H-10→L (31%)<br>H-4→L (12%) |

**-$CH_3$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.34 | 0.11 | H→L (98%) |
| 2 | 1.95 | 0.40 | H-1→L (94%) |
| 3 | 2.69 | 0.32 | H→L+1 (56%)<br>H-3→L (35%) |
| 4 | 2.92 | 0.13 | H-2→L (70%)<br>H-9→L (12%) |
| 5 | 3.04 | 0.17 | H-9→L (67%)<br>H-12→L (14%) |
| 6 | 3.07 | 1.73 | H-3→L (51%)<br>H→L+1 (29%) |
| 7 | 3.28 | 0.00 | H-10→L (89%) |
| 8 | 3.32 | 0.03 | H-7→L (50%)<br>H-6→L (34%) |
| 9 | 3.32 | 0.00 | H-6→L (57%)<br>H-7→L (36%) |
| 10 | 3.52 | 0.01 | H-12→L (79%)<br>H-9→L (15%) |

**-$C_2H_5$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.32 | 0.11 | H→L (98%) |
| 2 | 1.94 | 0.47 | H-1→L (93%) |
| 3 | 2.65 | 0.35 | H→L+1 (57%)<br>H-3→L (28%) |
| 4 | 2.91 | 0.31 | H-2→L (72%) |
| 5 | 3.03 | 0.02 | H-9→L (73%)<br>H-12→L (13%)<br>H-2→L (10%) |
| 6 | 3.04 | 1.59 | H-3→L (62%)<br>H→L+1 (27%) |
| 7 | 3.27 | 0.01 | H-10→L (93%) |
| 8 | 3.28 | 0.00 | H-6→L (89%) |
| 9 | 3.36 | 0.02 | H-7→L (88%) |
| 10 | 3.51 | 0.01 | H-12→L (80%)<br>H-9→L (14%) |

**-$C_3H_7$**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.37 | 0.13 | H→L (98%) |
| 2 | 1.97 | 0.52 | H-1→L (93%) |
| 3 | 2.69 | 0.25 | H→L+1 (50%)<br>H-3→L (36%) |
| 4 | 2.92 | 0.06 | H-2→L (71%)<br>H-9→L (13%) |
| 5 | 3.00 | 0.03 | H-9→L (68%)<br>H-2→L (11%)<br>H-12→L (10%) |
| 6 | 3.04 | 1.70 | H-3→L (46%)<br>H→L+1 (37%) |
| 7 | 3.26 | 0.07 | H-10→L (87%) |
| 8 | 3.31 | 0.00 | H-6→L (92%) |
| 9 | 3.35 | 0.04 | H-7→L (82%) |
| 10 | 3.49 | 0.01 | H-12→L (85%)<br>H-9→L (12%) |

### S4.2 different solvents, H-terminated 6T, cc-pVDZ

***in vacuo***

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.46 | 0.10 | H→L (97%) |
| 2 | 2.03 | 0.32 | H-1→L (95%) |
| 3 | 2.76 | 0.43 | H→L+1 (63%)<br>H-3→L (28%) |
| 4 | 3.01 | 0.02 | H-2→L (85%) |
| 5 | 3.10 | 0.01 | H-9→L (74%)<br>H-12→L (14%) |
| 6 | 3.12 | 2.12 | H-3→L (67%)<br>H→L+1 (26%) |
| 7 | 3.43 | 0.00 | H-10→L (61%)<br>H-6→L (28%) |
| 8 | 3.54 | 0.01 | H-1→L+1 (71%)<br>H→L+2 (19%) |
| 9 | 3.59 | 0.01 | H-7→L (73%)<br>H-5→L (14%) |
| 10 | 3.61 | 0.01 | H-6→L (51%)<br>H-10→L (31%)<br>H-4→L (12%) |

**benzene (apolar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.39 | 0.13 | H→L (97%) |
| 2 | 1.97 | 0.56 | H-1→L (94%) |
| 3 | 2.70 | 0.48 | H→L+1 (63%)<br>H-3→L (28%) |
| 4 | 2.96 | 2.26 | H-3→L (67%)<br>H→L+1 (25%) |
| 5 | 2.96 | 0.02 | H-2→L (84%) |
| 6 | 3.04 | 0.01 | H-9→L (73%)<br>H-12→L (12%) |
| 7 | 3.38 | 0.00 | H-10→L (68%)<br>H-6→L (21%) |
| 8 | 3.44 | 0.01 | H-1→L+1 (68%)<br>H→L+2 (24%) |
| 9 | 3.58 | 0.00 | H-7→L (68%)<br>H-5→L (16%)<br>H-12→L (11%) |
| 10 | 3.59 | 0.01 | H-6→L (56%)<br>H-10→L (22%)<br>H-4→L (16%) |

**chloroform (semi-polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.39 | 0.13 | H→L (97%) |
| 2 | 1.97 | 0.58 | H-1→L (94%) |
| 3 | 2.70 | 0.46 | H→L+1 (62%) |
| | | | H-3→L (29%) |
| 4 | 2.95 | 0.02 | H-2→L (76%) |
| | | | H-9→L (12%) |
| 5 | 2.97 | 2.24 | H-3→L (65%) |
| | | | H→L+1 (26%) |
| 6 | 3.01 | 0.01 | H-9→L (66%) |
| | | | H-2→L (14%) |
| | | | H-12→L (10%) |
| 7 | 3.35 | 0.00 | H-10→L (69%) |
| | | | H-6→L (18%) |
| 8 | 3.45 | 0.01 | H-1→L+1 (67%) |
| | | | H→L+2 (24%) |
| 9 | 3.58 | 0.00 | H-7→L (60%) |
| | | | H-12→L (16%) |
| | | | H-5→L (16%) |
| 10 | 3.60 | 0.01 | H-6→L (58%) |
| | | | H-4→L (19%) |
| | | | H-10→L (17%) |

**nitromethane (polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.39 | 0.14 | H→L (97%) |
| 2 | 1.97 | 0.58 | H-1→L (95%) |
| 3 | 2.71 | 0.44 | H→L+1 (61%) |
| | | | H-3→L (30%) |
| 4 | 2.94 | 0.00 | H-9→L (46%) |
| | | | H-2→L (35%) |
| | | | H-11→L (12%) |
| 5 | 2.98 | 0.03 | H-2→L (55%) |
| | | | H-9→L (30%) |
| 6 | 2.99 | 2.21 | H-3→L (64%) |
| | | | H→L+1 (27%) |
| 7 | 3.31 | 0.01 | H-10→L (65%) |
| | | | H-6→L (17%) |
| | | | H-8→L (14%) |
| 8 | 3.46 | 0.01 | H-1→L+1 (66%) |
| | | | H→L+2 (25%) |
| 9 | 3.58 | 0.00 | H-7→L (41%) |
| | | | H-11→L (25%) |
| | | | H-12→L (20%) |
| | | | H-5→L (12%) |
| 10 | 3.62 | 0.01 | H-6→L (56%) |
| | | | H-4→L (22%) |
| | | | H-10→L (13%) |

### S4.3 different solvents, $CH_3$-functionalized 6T, cc-pVDZ

***in vacuo***

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.34 | 0.11 | H→L (98%) |
| 2 | 1.95 | 0.40 | H-1→L (94%) |
| 3 | 2.69 | 0.32 | H→L+1 (56%) |
| | | | H-3→L (35%) |
| 4 | 2.92 | 0.13 | H-2→L (70%) |
| | | | H-9→L (12%) |
| 5 | 3.04 | 0.17 | H-9→L (67%) |
| | | | H-12→L (14%) |
| 6 | 3.07 | 1.73 | H-3→L (51%) |
| | | | H→L+1 (29%) |
| 7 | 3.28 | 0.00 | H-10→L (89%) |
| 8 | 3.32 | 0.03 | H-7→L (50%) |
| | | | H-6→L (34%) |
| 9 | 3.32 | 0.00 | H-6→L (57%) |
| | | | H-7→L (36%) |
| 10 | 3.52 | 0.01 | H-12→L (79%) |
| | | | H-9→L (15%) |

**benzene (apolar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.29 | 0.14 | H→L (98%) |
| 2 | 1.88 | 0.71 | H-1→L (94%) |
| 3 | 2.62 | 0.41 | H→L+1 (59%) |
| | | | H-3→L (32%) |
| 4 | 2.89 | 0.67 | H-2→L (45%) |
| | | | H-3→L (24%) |
| | | | H-9→L (11%) |
| 5 | 2.92 | 1.46 | H-3→L (36%) |
| | | | H-2→L (27%) |
| | | | H→L+1 (22%) |
| 6 | 3.00 | 0.02 | H-9→L (67%) |
| | | | H-2→L (16%) |
| | | | H-12→L (12%) |
| 7 | 3.26 | 0.00 | H-10→L (92%) |
| 8 | 3.34 | 0.01 | H-7→L (86%) |
| 9 | 3.36 | 0.00 | H-6→L (91%) |
| 10 | 3.43 | 0.01 | H-1→L+1 (72%) |
| | | | H→L+2 (19%) |

**chloroform (semi-polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.30 | 0.15 | H→L (98%) |
| 2 | 1.88 | 0.73 | H-1→L (94%) |
| 3 | 2.63 | 0.41 | H→L+1 (58%) |
| | | | H-3→L (32%) |
| 4 | 2.88 | 0.21 | H-2→L (51%) |
| | | | H-9→L (20%) |
| | | | H-3→L (13%) |
| 5 | 2.92 | 1.84 | H-3→L (46%) |
| | | | H→L+1 (29%) |
| | | | H-2→L (14%) |
| 6 | 2.97 | 0.03 | H-9→L (54%) |
| | | | H-2→L (23%) |
| | | | H-12→L (11%) |
| 7 | 3.24 | 0.01 | H-10→L (94%) |
| 8 | 3.36 | 0.01 | H-7→L (81%) |
| | | | H-6→L (11%) |
| 9 | 3.38 | 0.00 | H-6→L (84%) |
| | | | H-7→L (11%) |
| 10 | 3.43 | 0.01 | H-1→L+1 (72%) |
| | | | H→L+2 (18%) |

**nitromethane (polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.31 | 0.15 | H→L (98%) |
| 2 | 1.88 | 0.75 | H-1→L (94%) |
| 3 | 2.63 | 0.38 | H→L+1 (57%) |
| | | | H-3→L (33%) |
| 4 | 2.86 | 0.05 | H-2→L (41%) |
| | | | H-8→L (35%) |
| 5 | 2.93 | 1.88 | H-3→L (46%) |
| | | | H→L+1 (32%) |
| | | | H-2→L (12%) |
| 6 | 2.94 | 0.10 | H-8→L (41%) |
| | | | H-2→L (35%) |
| 7 | 3.20 | 0.02 | H-10→L (93%) |
| 8 | 3.37 | 0.01 | H-7→L (79%) |
| | | | H-6→L (13%) |
| 9 | 3.41 | 0.00 | H-6→L (79%) |
| | | | H-7→L (15%) |
| 10 | 3.44 | 0.01 | H-12→L (65%) |
| | | | H-11→L (16%) |
| | | | H-8→L (12%) |

### S4.4 different solvents, H-terminated 6T, cc-pVTZ

***in vacuo***

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.38 | 0.09 | H→L (97%) |
| 2 | 1.95 | 0.33 | H-1→L (95%) |
| 3 | 2.71 | 0.41 | H→L+1 (63%)<br>H-3→L (27%) |
| 4 | 2.93 | 0.02 | H-2→L (89%) |
| 5 | 3.07 | 2.01 | H-3→L (67%)<br>H→L+1 (25%) |
| 6 | 3.08 | 0.00 | H-9→L (75%)<br>H-12→L (16%) |
| 7 | 3.34 | 0.00 | H-10→L (56%)<br>H-6→L (32%) |
| 8 | 3.46 | 0.00 | H-1→L+1 (67%)<br>H→L+2 (20%) |
| 9 | 3.50 | 0.01 | H-7→L (69%)<br>H-5→L (16%) |
| 10 | 3.51 | 0.01 | H-6→L (46%)<br>H-10→L (34%)<br>H-4→L (13%) |

**benzene (apolar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.31 | 0.12 | H→L (97%) |
| 2 | 1.89 | 0.60 | H-1→L (94%) |
| 3 | 2.65 | 0.46 | H→L+1 (64%)<br>H-3→L (27%) |
| 4 | 2.88 | 0.03 | H-2→L (89%) |
| 5 | 2.91 | 2.18 | H-3→L (66%)<br>H→L+1 (25%) |
| 6 | 3.01 | 0.00 | H-9→L (76%)<br>H-12→L (14%) |
| 7 | 3.28 | 0.00 | H-10→L (64%)<br>H-6→L (23%) |
| 8 | 3.36 | 0.01 | H-1→L+1 (67%)<br>H→L+2 (25%) |
| 9 | 3.49 | 0.01 | H-7→L (68%)<br>H-5→L (19%) |
| 10 | 3.49 | 0.01 | H-6→L (52%)<br>H-10→L (23%)<br>H-4→L (18%) |

**chloroform (semi-polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.31 | 0.13 | H→L (97%) |
| 2 | 1.88 | 0.61 | H-1→L (94%) |
| 3 | 2.66 | 0.43 | H→L+1 (62%) |
| | | | H-3→L (28%) |
| 4 | 2.87 | 0.03 | H-2→L (89%) |
| 5 | 2.92 | 2.15 | H-3→L (64%) |
| | | | H→L+1 (26%) |
| 6 | 2.98 | 0.00 | H-9→L (76%) |
| | | | H-12→L (12%) |
| 7 | 3.25 | 0.01 | H-10→L (65%) |
| | | | H-6→L (19%) |
| 8 | 3.38 | 0.01 | H-1→L+1 (66%) |
| | | | H→L+2 (25%) |
| 9 | 3.49 | 0.01 | H-7→L (63%) |
| | | | H-5→L (19%) |
| | | | H-12→L (13%) |
| 10 | 3.50 | 0.01 | H-6→L (53%) |
| | | | H-4→L (21%) |
| | | | H-10→L (18%) |

**nitromethane (polar)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.32 | 0.13 | H→L (97%) |
| 2 | 1.89 | 0.62 | H-1→L (94%) |
| 3 | 2.67 | 0.41 | H→L+1 (61%) |
| | | | H-3→L (30%) |
| 4 | 2.87 | 0.02 | H-2→L (87%) |
| 5 | 2.93 | 0.01 | H-9→L (73%) |
| 6 | 2.94 | 2.12 | H-3→L (62%) |
| | | | H→L+1 (27%) |
| 7 | 3.21 | 0.01 | H-10→L (58%) |
| | | | H-8→L (19%) |
| | | | H-6→L (17%) |
| 8 | 3.39 | 0.01 | H-1→L+1 (65%) |
| | | | H→L+2 (26%) |
| 9 | 3.50 | 0.00 | H-7→L (48%) |
| | | | H-12→L (22%) |
| | | | H-5→L (17%) |
| | | | H-11→L (11%) |
| 10 | 3.52 | 0.01 | H-6→L (52%) |
| | | | H-4→L (25%) |
| | | | H-10→L (12%) |

### S4.5 *in vacuo*, $CH_3$-functionalized 6T, different basis sets

**cc-pVDZ**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.34 | 0.11 | H→L (98%) |
| 2 | 1.95 | 0.40 | H-1→L (94%) |
| 3 | 2.69 | 0.32 | H→L+1 (56%)<br>H-3→L (35%) |
| 4 | 2.92 | 0.13 | H-2→L (70%)<br>H-9→L (12%) |
| 5 | 3.04 | 0.17 | H-9→L (67%)<br>H-12→L (14%) |
| 6 | 3.07 | 1.73 | H-3→L (51%)<br>H→L+1 (29%) |
| 7 | 3.28 | 0.00 | H-10→L (89%) |
| 8 | 3.32 | 0.03 | H-7→L (50%)<br>H-6→L (34%) |
| 9 | 3.32 | 0.00 | H-6→L (57%)<br>H-7→L (36%) |
| 10 | 3.52 | 0.01 | H-12→L (79%)<br>H-9→L (15%) |

**6-31G(d,p)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.34 | 0.11 | H→L (98%) |
| 2 | 1.94 | 0.42 | H-1→L (94%) |
| 3 | 2.69 | 0.26 | H→L+1 (53%)<br>H-3→L (38%) |
| 4 | 2.91 | 0.10 | H-2→L (71%)<br>H-9→L (13%) |
| 5 | 3.04 | 0.18 | H-9→L (65%)<br>H-12→L (14%) |
| 6 | 3.06 | 1.79 | H-3→L (49%)<br>H→L+1 (32%) |
| 7 | 3.30 | 0.00 | H-10→L (88%) |
| 8 | 3.32 | 0.00 | H-6→L (92%) |
| 9 | 3.33 | 0.03 | H-7→L (82%) |
| 10 | 3.52 | 0.01 | H-12→L (79%)<br>H-9→L (16%) |

**6-31+G(d,p)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.28 | 0.10 | H→L (98%) |
| 2 | 1.88 | 0.45 | H-1→L (94%) |
| 3 | 2.65 | 0.27 | H→L+1 (54%)<br>H-3→L (36%) |
| 4 | 2.85 | 0.10 | H-2→L (80%) |
| 5 | 3.01 | 1.81 | H-3→L (51%)<br>H→L+1 (33%) |
| 6 | 3.03 | 0.06 | H-9→L (81%)<br>H-12→L (11%) |
| 7 | 3.22 | 0.01 | H-10→L (66%)<br>H-7→L (27%) |
| 8 | 3.24 | 0.02 | H-6→L (80%)<br>H-7→L (12%) |
| 9 | 3.24 | 0.02 | H-7→L (51%)<br>H-10→L (30%)<br>H-6→L (11%) |
| 10 | 3.49 | 0.00 | H-1→L+1 (72%)<br>H→L+2 (15%) |

**6-31++G(d,p)**

| # | $E$ (eV) | OS | transition (weight) |
|---|---|---|---|
| 1 | 1.28 | 0.10 | H→L (98%) |
| 2 | 1.88 | 0.45 | H-1→L (94%) |
| 3 | 2.65 | 0.27 | H→L+1 (54%)<br>H-3→L (36%) |
| 4 | 2.85 | 0.11 | H-2→L (80%) |
| 5 | 3.01 | 1.80 | H-3→L (51%)<br>H→L+1 (33%) |
| 6 | 3.03 | 0.06 | H-9→L (81%)<br>H-12→L (11%) |
| 7 | 3.22 | 0.01 | H-10→L (67%)<br>H-7→L (27%) |
| 8 | 3.24 | 0.03 | H-6→L (74%)<br>H-7→L (15%) |
| 9 | 3.24 | 0.02 | H-7→L (48%)<br>H-10→L (29%)<br>H-6→L (17%) |
| 10 | 3.49 | 0.00 | H-1→L+1 (72%)<br>H→L+2 (15%) |