

Photophysical properties of quinoxaline-fused [7]carbohelicene derivatives

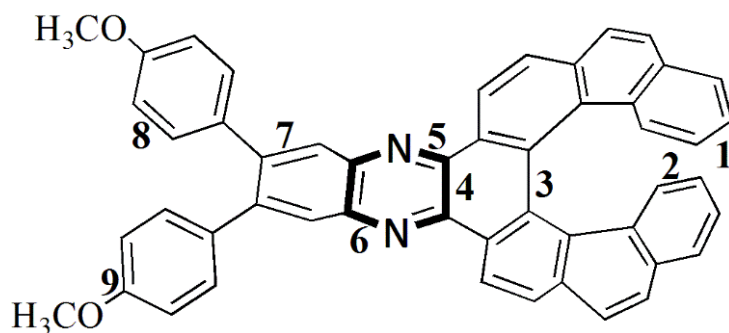
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Table S1. The main concerned bond length for compound **4** between experiment and calculation.



| Bond | B3LYP | Experiment | Difference |
|------|-------|------------|------------|
| 1 | 1.407 | 1.405 | 0.002 |
| 2 | 1.382 | 1.379 | 0.003 |
| 3 | 1.479 | 1.479 | 0.000 |
| 4 | 1.439 | 1.438 | 0.001 |
| 5 | 1.330 | 1.333 | -0.003 |
| 6 | 1.352 | 1.355 | -0.003 |
| 7 | 1.383 | 1.369 | 0.014 |
| 8 | 1.397 | 1.377 | 0.020 |
| 9 | 1.365 | 1.370 | 0.005 |

Note: the difference is equal to calculation value minus experimental value

Table S2. Computed absorption wavelengths (nm) using the B3LYP functional at the different basis sets level for compound **2** along with the experimental values.

| Basis set | Band 1 | Band 2 | Band 3 | Band 4 |
|-----------------|--------|--------|--------|--------|
| 6-31G(d) | 278.90 | 313.25 | 341.40 | 419.99 |
| 6-31+G(d) | 282.49 | 316.45 | 346.13 | 424.85 |
| 6-31++G(d,p) | 282.74 | 316.54 | 346.24 | 424.78 |
| 6-311++G(d,p) | 283.80 | 317.94 | 348.20 | 426.72 |
| 6-311++G(2d,2p) | 284.42 | 318.48 | 349.18 | 427.27 |
| exp | 276 | 332 | 366 | 427 |

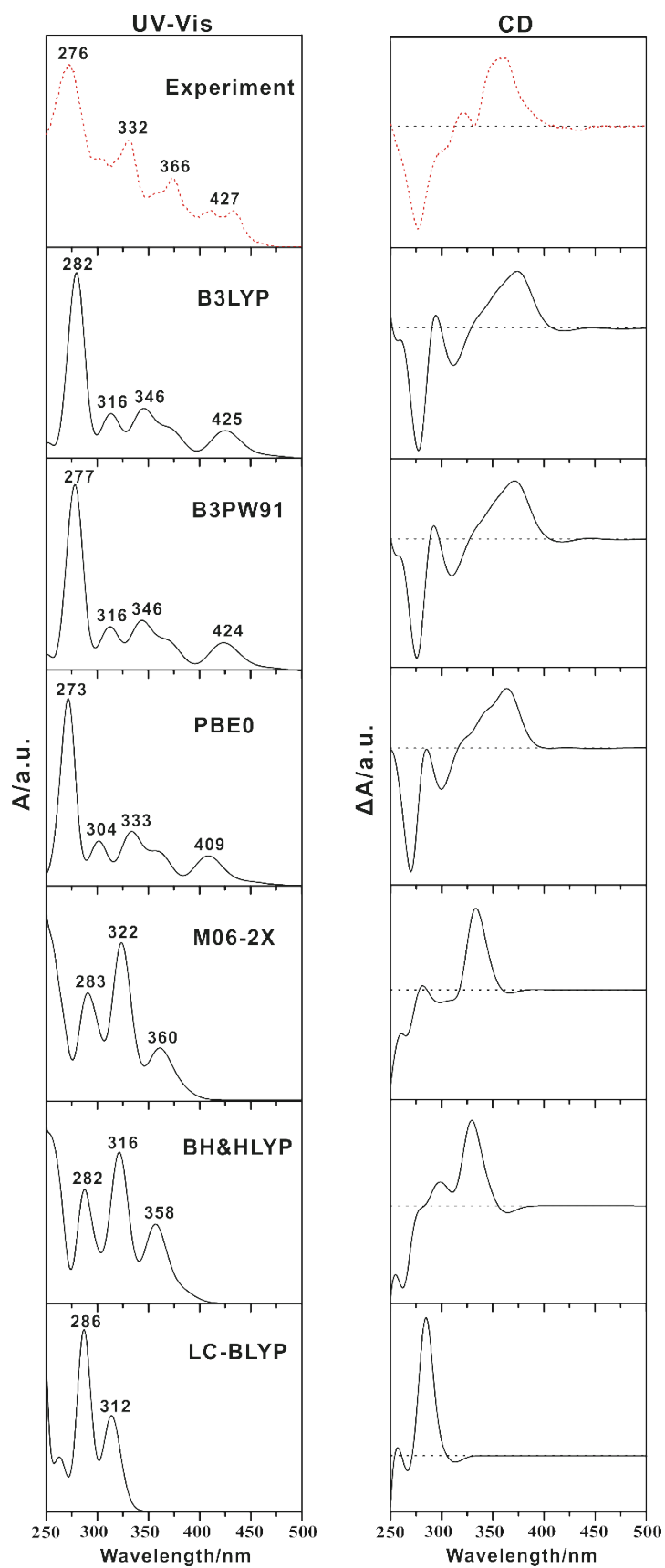


Figure S1. Calculated UV-Vis (left) and CD (right) spectra of compound **2** using six different DFT functionals along with the experimental spectra.

Table S3. Computed HOMO and LUMO energy level and corresponding energy gaps (E_g =LUMO-HOMO) in eV using different functionals at 6-31+G(d) basis set level for compound **2**.

| Functional | HUMO | LUMO | E_g |
|------------|--------|--------|-------|
| B3LYP | -5.757 | -2.574 | 3.183 |
| PBE0 | -5.961 | -2.480 | 3.481 |
| B3PW91 | -5.819 | -2.628 | 3.191 |
| M06-2X | -6.896 | -1.835 | 5.061 |
| BH&HLYP | -6.537 | -1.603 | 4.934 |
| LC-BLYP | -8.226 | -0.481 | 7.745 |

Table S4. The calculated excitation energies, oscillator strengths and rotational strengths for compound **2** in the gas phase at the TDB3LYP/ 6-31+G(d) level.

| states | eV | λ^a | f^b | Rlength ^c | Rvelocity ^c |
|--------|--------|-------------|--------|----------------------|------------------------|
| 1 | 2.6440 | 468.92 | 0.0224 | 5.5739 | 5.1048 |
| 2 | 2.8851 | 429.74 | 0.0112 | -46.2693 | -45.2348 |
| 3 | 2.9183 | 424.85 | 0.1891 | 57.2984 | 54.9835 |
| 4 | 3.2810 | 377.88 | 0.0005 | -0.0633 | -0.2286 |
| 5 | 3.2991 | 375.81 | 0.0674 | -308.9714 | -309.9281 |
| 6 | 3.3071 | 374.90 | 0.0693 | 53.0994 | 52.4732 |
| 7 | 3.3946 | 365.23 | 0.0832 | -3.5566 | -3.5030 |
| 8 | 3.4951 | 354.74 | 0.0076 | -126.4121 | -124.9949 |
| 9 | 3.5685 | 347.44 | 0.0692 | -191.9522 | -191.1530 |
| 10 | 3.5820 | 346.13 | 0.2068 | 211.4651 | 205.9730 |
| 11 | 3.6540 | 339.31 | 0.0080 | -46.5211 | -43.4195 |
| 12 | 3.6855 | 336.41 | 0.0844 | -28.7331 | -28.0954 |
| 13 | 3.9180 | 316.45 | 0.2195 | 59.3692 | 57.4197 |
| 14 | 4.0151 | 308.79 | 0.0742 | 78.5611 | 75.1716 |
| 15 | 4.0341 | 307.34 | 0.0435 | 57.8225 | 57.9084 |
| 16 | 4.0579 | 305.54 | 0.0247 | -15.2280 | -15.2438 |
| 17 | 4.1594 | 298.08 | 0.0038 | -10.5911 | -9.6629 |
| 18 | 4.1642 | 297.74 | 0.0044 | 10.5572 | 10.8161 |
| 19 | 4.2477 | 291.88 | 0.0157 | -22.4081 | -22.3610 |
| 20 | 4.2734 | 290.13 | 0.0164 | -78.0292 | -77.1421 |
| 21 | 4.3173 | 287.18 | 0.0047 | -1.8169 | -2.0775 |
| 22 | 4.3442 | 285.40 | 0.0326 | -136.8769 | -133.1782 |
| 23 | 4.3890 | 282.49 | 0.7815 | 259.6704 | 254.5679 |
| 24 | 4.4281 | 280.00 | 0.0078 | 4.4532 | 4.0056 |
| 25 | 4.4535 | 278.40 | 0.3126 | 298.5076 | 292.8781 |
| 26 | 4.4936 | 275.91 | 0.0988 | -119.4684 | -112.3997 |
| 27 | 4.5204 | 274.28 | 0.0349 | 30.4146 | 30.5501 |
| 28 | 4.5659 | 271.54 | 0.3065 | 229.5874 | 220.4800 |
| 29 | 4.5846 | 270.44 | 0.0369 | -9.2351 | -8.3509 |
| 30 | 4.7298 | 262.14 | 0.0010 | -18.0344 | -19.9286 |
| 31 | 4.7745 | 259.68 | 0.0095 | -46.7129 | -43.8157 |
| 32 | 4.7990 | 258.35 | 0.0031 | 42.5221 | 38.4494 |
| 33 | 4.8537 | 255.44 | 0.0023 | 44.1085 | 44.8482 |
| 34 | 4.8836 | 253.88 | 0.0291 | 4.2786 | 4.0528 |
| 35 | 4.8861 | 253.75 | 0.0209 | -5.1898 | -4.4951 |
| 36 | 4.9057 | 252.73 | 0.0026 | 31.8721 | 31.3515 |
| 37 | 4.9553 | 250.20 | 0.0466 | -14.3257 | -13.2494 |
| 38 | 4.9798 | 248.97 | 0.0055 | -12.4077 | -12.0278 |
| 39 | 4.9947 | 248.23 | 0.0012 | -15.4280 | -12.0929 |

| | | | | | |
|----|--------|--------|--------|-----------|-----------|
| 40 | 5.0903 | 243.57 | 0.0200 | -110.1612 | -106.9509 |
| 41 | 5.1060 | 242.82 | 0.0107 | -3.9865 | -4.1217 |
| 42 | 5.1659 | 240.00 | 0.0041 | 6.5592 | 6.3127 |
| 43 | 5.1684 | 239.89 | 0.0309 | -42.0964 | -39.9093 |
| 44 | 5.2035 | 238.27 | 0.0006 | 1.7824 | 1.9336 |
| 45 | 5.2075 | 238.09 | 0.0000 | -0.1136 | -0.0247 |
| 46 | 5.2152 | 237.73 | 0.0007 | 6.3266 | 4.7656 |
| 47 | 5.2533 | 236.01 | 0.0130 | 31.0118 | 31.8413 |
| 48 | 5.2641 | 235.53 | 0.0003 | 0.7014 | 1.2800 |
| 49 | 5.3123 | 233.39 | 0.0138 | -16.7621 | -16.5259 |
| 50 | 5.3147 | 233.28 | 0.0012 | 1.9467 | 1.7718 |
| 51 | 5.3380 | 232.27 | 0.0001 | 3.3390 | 3.8701 |
| 52 | 5.3414 | 232.12 | 0.0220 | -25.3855 | -23.4324 |
| 53 | 5.3547 | 231.54 | 0.0506 | 4.6474 | 4.4342 |
| 54 | 5.3696 | 230.90 | 0.0169 | 39.5927 | 38.1616 |
| 55 | 5.3933 | 229.88 | 0.0010 | 4.0598 | 3.9349 |
| 56 | 5.4053 | 229.37 | 0.0129 | -18.3724 | -16.9195 |
| 57 | 5.4072 | 229.30 | 0.0052 | -22.3822 | -21.8288 |
| 58 | 5.4309 | 228.29 | 0.0107 | -24.7518 | -24.4644 |
| 59 | 5.4401 | 227.91 | 0.0169 | 2.4085 | 2.4843 |
| 60 | 5.4525 | 227.39 | 0.1216 | -107.9398 | -105.0485 |

^a λ in nm. ^b Oscillator Strengths. ^c R values (in 10^{-40} esu²cm²) using the velocity-gauge representation and length-gauge representation of the electric dipole operator.

Table S5. Computed absorption wavelengths (λ in nm) as compared to experimental data (in parentheses), oscillator strengths (f), and major contribution for the studied compounds **1**, **3**, **4**, **5** and **6**.

| Compound | λ | f | Major contribution |
|----------|-------------|-------|--|
| 1 | 273.82(272) | 0.509 | HOMO-1 \rightarrow LUMO+3 (44%) HOMO-3 \rightarrow LUMO (13%) |
| | 311.91(303) | 0.015 | HOMO-3 \rightarrow LUMO+1 (55%) HOMO-1 \rightarrow LUMO+2 (42%) |
| | 374.34(373) | 0.104 | HOMO \rightarrow LUMO+1 (59%) HOMO-1 \rightarrow LUMO (25%) |
| 3 | 272.71(283) | 0.366 | HOMO-2 \rightarrow LUMO+5 (32%) HOMO-12 \rightarrow LUMO (19%) |
| | 301.46(335) | 0.128 | HOMO-1 \rightarrow LUMO+3 (44%) HOMO \rightarrow LUMO+5 (15%) |
| | 349.57(378) | 0.640 | HOMO-2 \rightarrow LUMO+1 (39%) HOMO \rightarrow LUMO+1 (29%) |
| | 438.13(445) | 0.416 | HOMO-1 \rightarrow LUMO (88%) HOMO \rightarrow LUMO+1 (9%) |
| 4 | 276.15(286) | 0.064 | HOMO-12 \rightarrow LUMO (33%) HOMO-8 \rightarrow LUMO+1 (14%) |
| | 308.78(333) | 0.251 | HOMO-8 \rightarrow LUMO (51%) HOMO-4 \rightarrow LUMO+2 (16%) |
| | 352.72(383) | 0.573 | HOMO \rightarrow LUMO+2 (51%) HOMO-1 \rightarrow LUMO+1 (22%) |
| | 449.65(450) | 0.571 | HOMO-1 \rightarrow LUMO (93%) |
| 5 | 287.72 | 0.478 | HOMO-1 \rightarrow LUMO+5 (48%) HOMO-2 \rightarrow LUMO+4 (15%) |
| | 312.87 | 0.302 | HOMO-8 \rightarrow LUMO (34%) HOMO \rightarrow LUMO+3 (31%) |
| | 359.21 | 0.579 | HOMO-1 \rightarrow LUMO+2 (52%) HOMO \rightarrow LUMO+1 (17%) |
| | 476.34 | 0.533 | HOMO \rightarrow LUMO (96%) |
| 6 | 285.74 | 0.408 | HOMO \rightarrow LUMO+7 (46%) HOMO-1 \rightarrow LUMO+5 (12%) |
| | 348.46 | 0.498 | HOMO-2 \rightarrow LUMO+3 (57%) HOMO \rightarrow LUMO+3 (14%) |
| | 456.00 | 0.412 | HOMO \rightarrow LUMO+1 (64%) HOMO-1 \rightarrow LUMO (34%) |

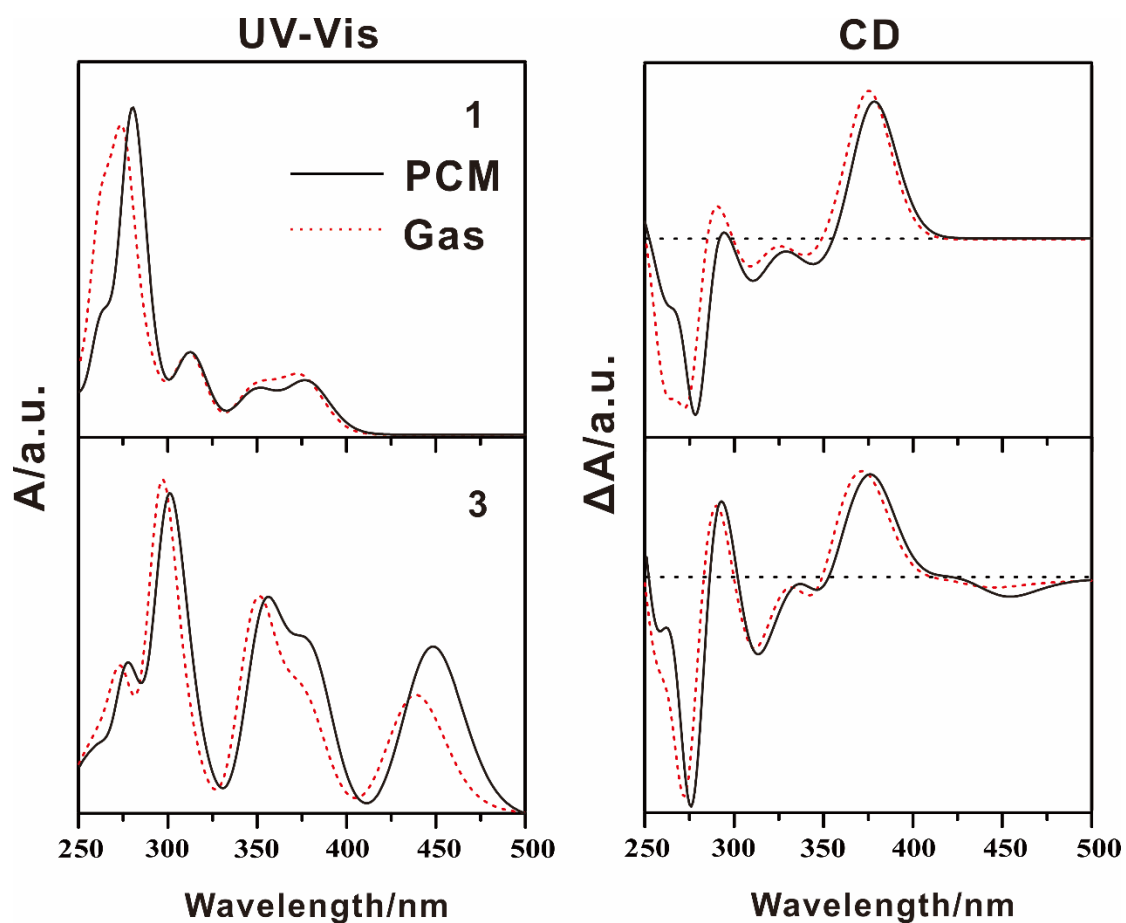
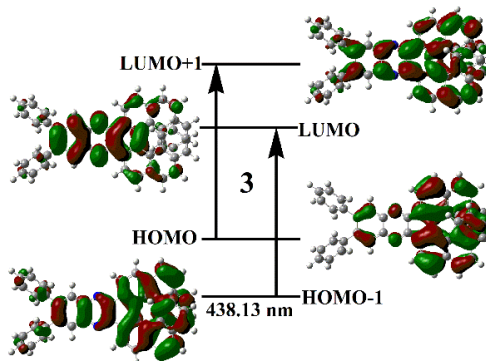
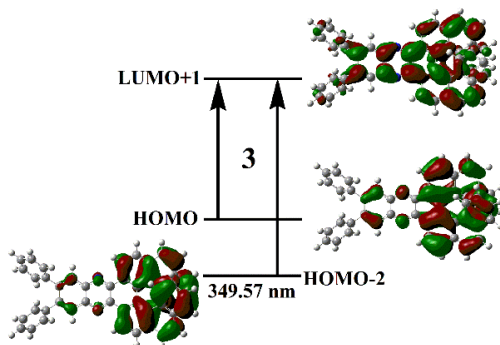
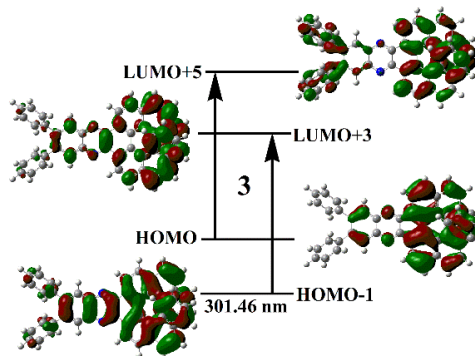
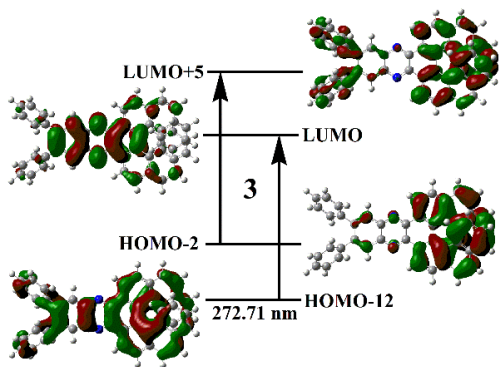
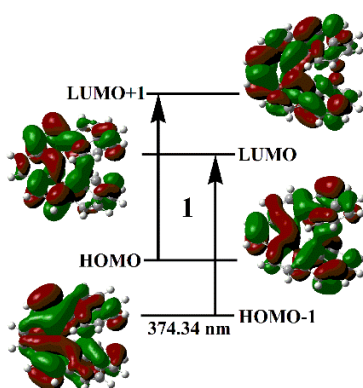
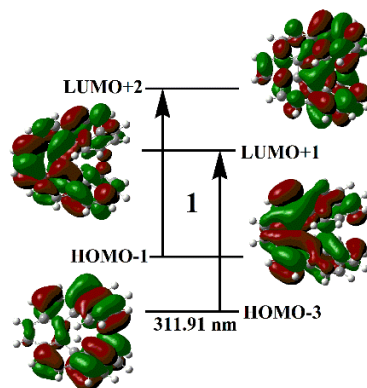
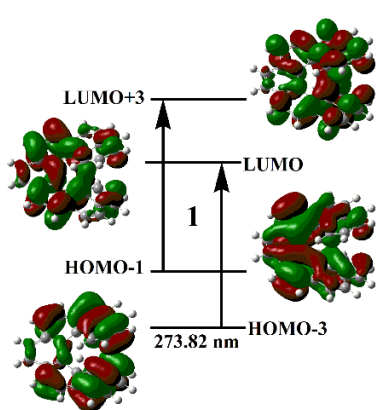


Figure S2. Calculated UV-Vis (left) and CD (right) spectra in solution phases(THF) of **1** and **3** at the TDB3LYP/6-31+G(d) level of theory along with gas phases UV-Vis and CD (red dash line).



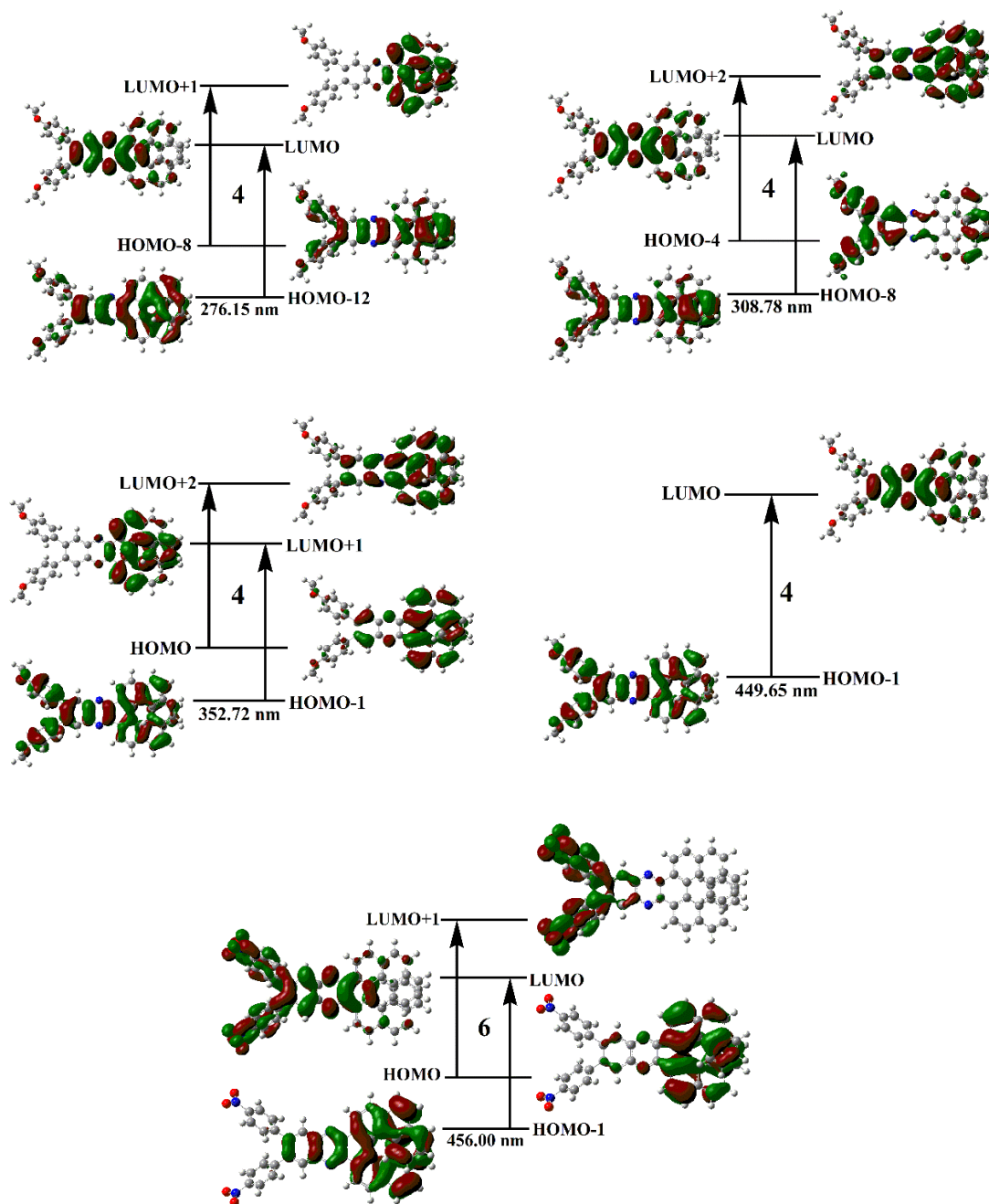
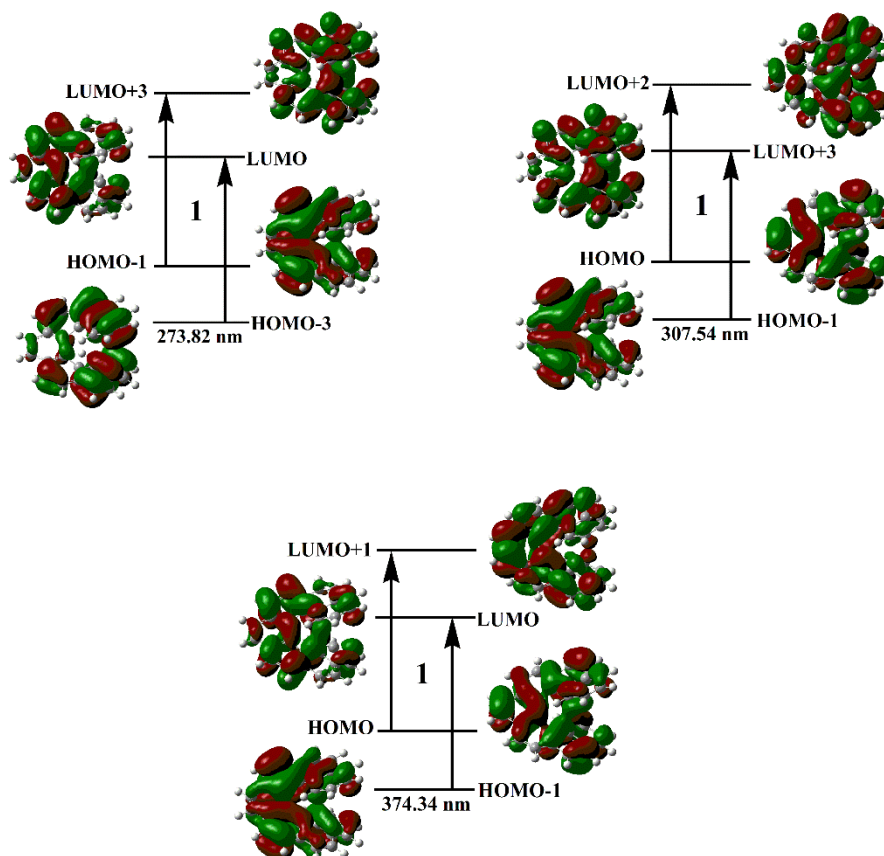


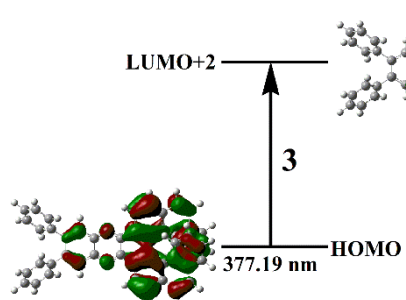
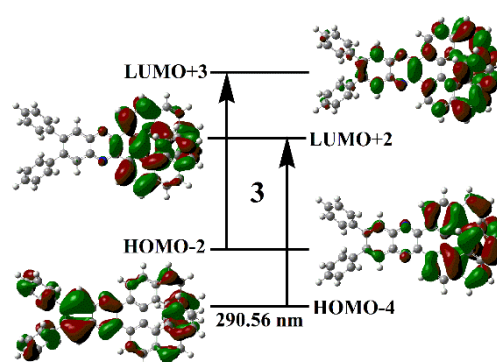
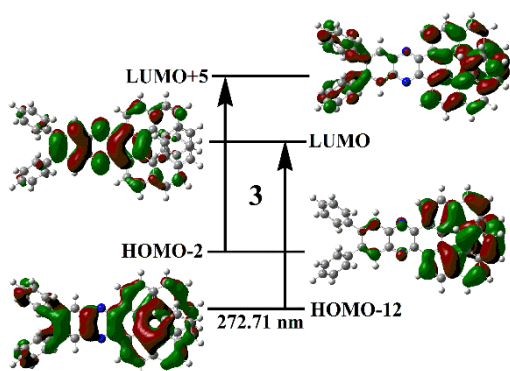
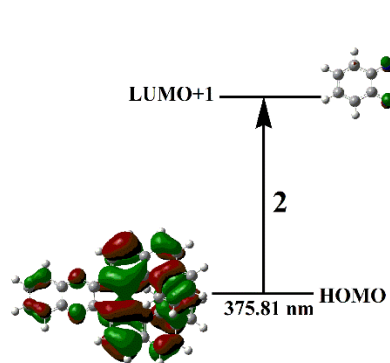
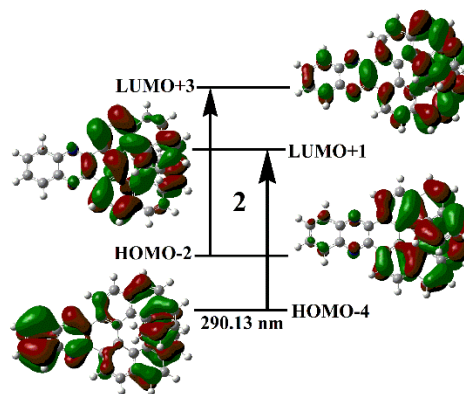
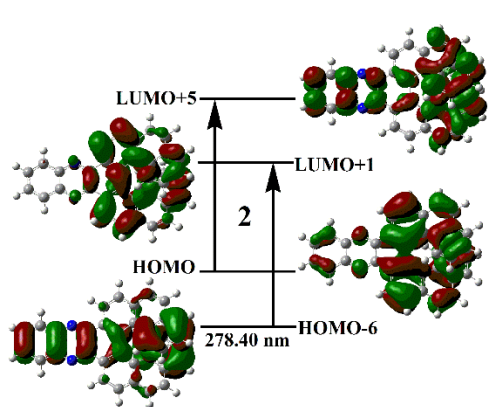
Figure S3. Molecular orbital isosurfaces involved in the main electron transitions of compounds **1**, **3**, **4** and **6** at the TDB3LYP/6-31+G(d) level of theory.

Table S6. Computed HOMO and LUMO energy level and corresponding energy gaps

(E_g =LUMO-HOMO) in eV at the TDB3LYP/6-31G(d,p) level for compounds 1-6.

| Compound | HOMO | LUMO | E_g |
|----------|--------|--------|-------|
| 1 | -5.371 | -1.508 | 3.863 |
| 2 | -5.484 | -2.272 | 3.212 |
| 3 | -5.454 | -2.295 | 3.159 |
| 4 | -5.377 | -2.198 | 3.179 |
| 5 | -5.114 | -2.099 | 3.015 |
| 6 | -5.767 | -2.844 | 2.923 |





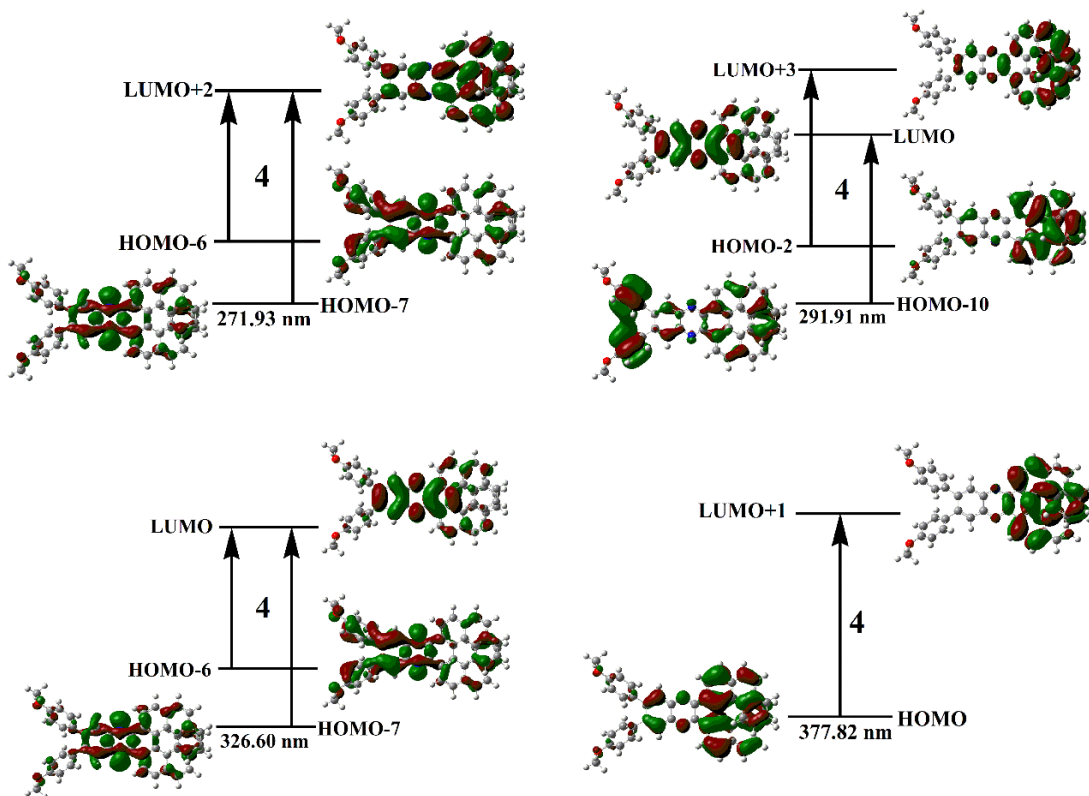
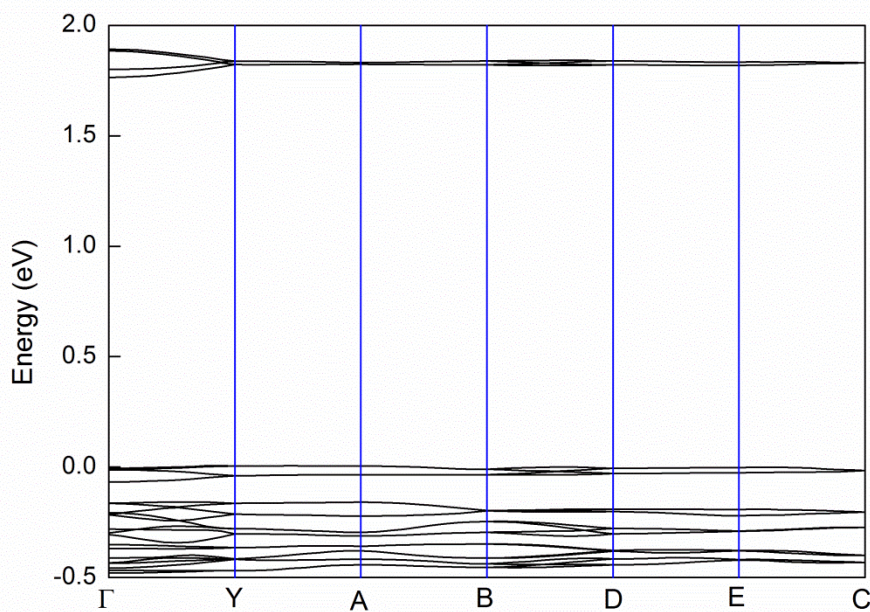


Figure S4. Molecular orbitals involved into the main CD transition of compounds 1-4.



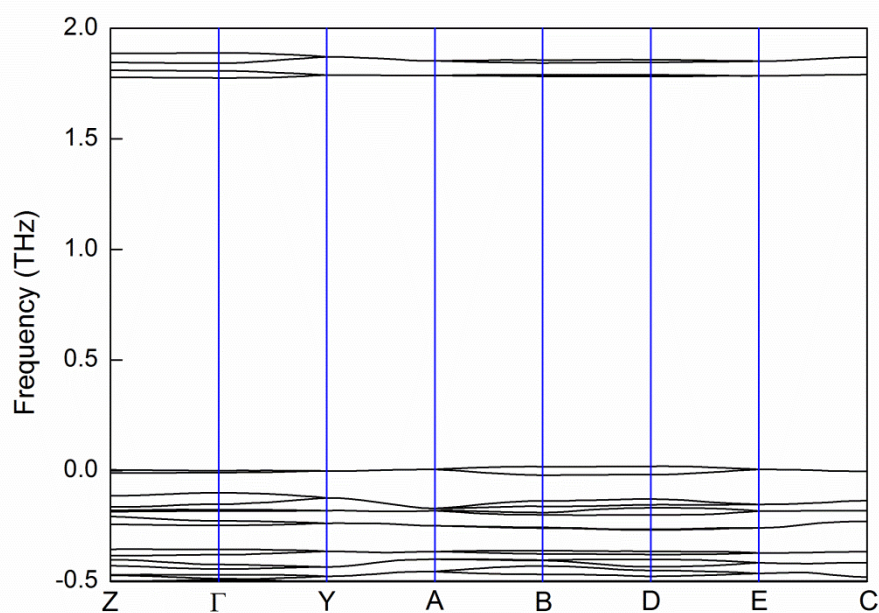


Figure S5. Calculated band structure of the crystal for compound **4** in its racemate (top) and enantiomer crystals (bottom). The high symmetry points in racemate are $\Gamma = (0, 0, 0)$, $Y = (0, 0.5, 0)$, $A = (-0.5, 0.5, 0.5)$, $B = (-0.5, 0, 0)$, $D = (-0.5, 0, 0.5)$, $E = (-0.5, 0.5, 0.5)$ and $X = (0, 0.5, 0.5)$. The high symmetry points in enantiomer crystals are $Z = (0, 0, 0.5)$, $\Gamma = (0, 0, 0)$, $Y = (0, 0.5, 0)$, $A = (-0.5, 0.5, 0.5)$, $B = (-0.5, 0, 0)$, $D = (-0.5, 0, 0.5)$, $E = (-0.5, 0.5, 0.5)$ and $X = (0, 0.5, 0.5)$.