Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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*Supporting Information*

# On the Design of Atropisomer-Separable Photochromic Diarylethene-based Metal-organic Framework Linkers

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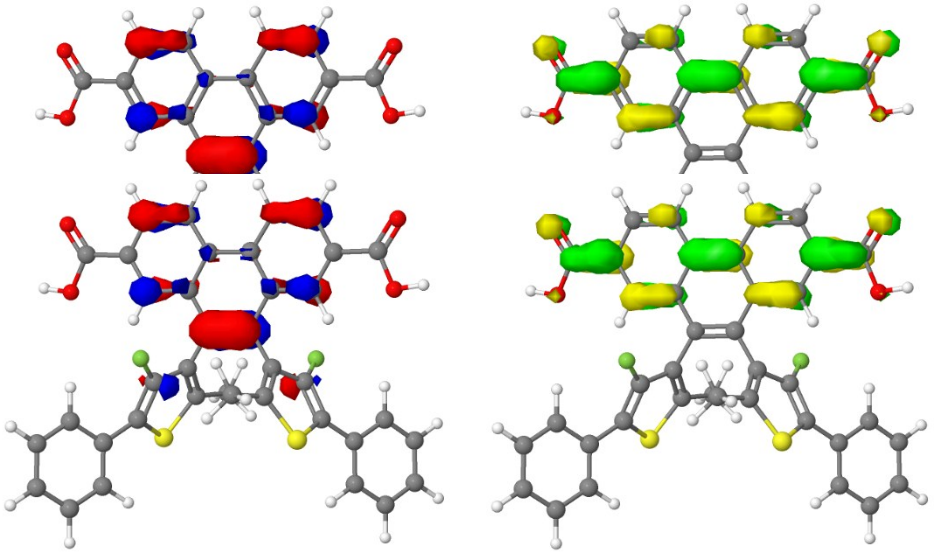
Table S1. Distances of potentially photoactive carbon atoms in each molecule, the excitation energy and oscillator strength of the lowest energy electronic transition, as well as the individual electronic transition components, and their associated CI expansion coefficients, which comprise the lowest energy transition in the open form of each molecule. Highlighted transitions are the major contributor to the excitation.

| Molecule | Photoactive C-C Distance (Å) | Excitation Energy (nm) | Oscillator Strength | Electronic Transitions | CI Expansion Coefficients |
|---|---|---|---|---|---|
| 1H | 3.679 | 312.85 | 0.0565 | HOMO-4 → LUMO | -0.12231 |
| | | | | HOMO-3 → LUMO+1 | 0.25866 |
| | | | | HOMO-2 → LUMO | 0.55967 |
| | | | | HOMO → LUMO | -0.27451 |
| 1F | 3.645 | 308.89 | 0.0469 | HOMO-4 → LUMO | -0.13382 |
| | | | | HOMO-3 → LUMO+1 | 0.28594 |
| | | | | HOMO-2 → LUMO | 0.56146 |
| | | | | HOMO → LUMO | -0.23242 |
| 1Cl | 3.626 | 308.86 | 0.0440 | HOMO-4 → LUMO | -0.11654 |
| | | | | HOMO-3 → LUMO+1 | 0.28683 |
| | | | | HOMO-1 → LUMO | 0.46981 |
| | | | | HOMO → LUMO | 0.38747 |
| 1Br | 3.646 | 308.72 | 0.0432 | HOMO-4 → LUMO | -0.11365 |
| | | | | HOMO-3 → LUMO+1 | 0.28667 |
| | | | | HOMO-2 → LUMO | 0.47514 |
| | | | | HOMO → LUMO | -0.38064 |
| 1I | 3.589 | 310.13 | 0.0423 | HOMO-4 → LUMO | -0.11458 |
| | | | | HOMO-3 → LUMO+1 | -0.28142 |
| | | | | HOMO-1 → LUMO | 0.39880 |
| | | | | HOMO → LUMO | 0.45890 |
| 1Me | 3.581 | 314.64 | 0.0552 | HOMO-4 → LUMO | -0.17467 |
| | | | | HOMO-3 → LUMO+1 | 0.24287 |
| | | | | HOMO-2 → LUMO | 0.50810 |
| | | | | HOMO → LUMO | -0.34817 |
| 1OMe | 3.675 | 318.30 | 0.0705 | HOMO-5 → LUMO+1 | -0.18896 |
| | | | | HOMO-4 → LUMO+1 | 0.15634 |
| | | | | HOMO-3 → LUMO | -0.25309 |
| | | | | HOMO-2 → LUMO | 0.51021 |
| | | | | HOMO → LUMO | 0.30074 |
| 2 | 3.711 | 307.95 | 0.0463 | HOMO-3 → LUMO+1 | 0.25272 |
| | | | | HOMO-3 → LUMO+3 | -0.12648 |
| | | | | HOMO-1 → LUMO | 0.53361 |
| | | | | HOMO → LUMO | 0.30852 |
| 3 | 3.685 | 310.42 | 0.0468 | HOMO-5 → LUMO+1 | 0.27407 |
| | | | | HOMO-3 → LUMO | 0.15461 |
| | | | | HOMO-2 → LUMO | 0.52405 |
| | | | | HOMO → LUMO | -0.30915 |

Table S2. Excitation energies and oscillator strength of lowest energy transition in the closed-form of each system. Also shown are the individual electronic transition components and associated CI expansion coefficients which comprise the lowest energy transition. Highlighted transitions are the major contributor to the excitation.

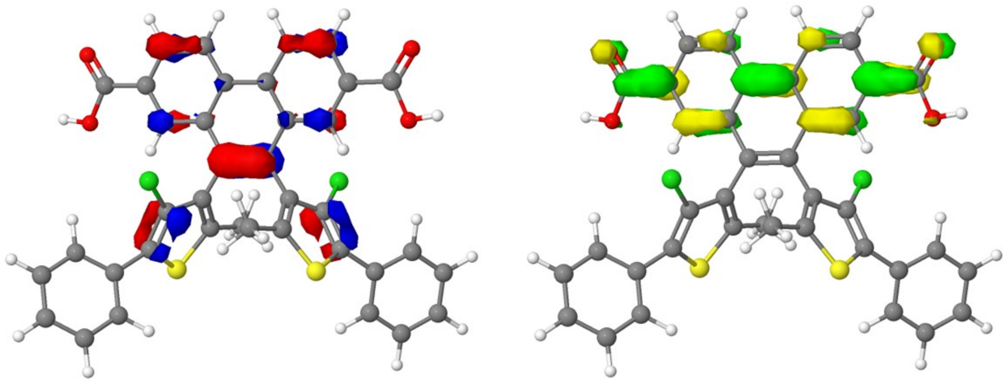
| Molecule | Excitation Energy (nm) | Oscillator Strength | Electronic Transitions | CI Expansion Coefficients |
|---|---|---|---|---|
| 1H | 625.5 | 0.2506 | HOMO → LUMO | 0.68818 |
| 1F | 654.8 | 0.255 | HOMO → LUMO | 0.69216 |
| 1Cl | 625.36 | 0.1939 | HOMO → LUMO | 0.69121 |
| 1Br | 629.99 | 0.1965 | HOMO → LUMO | 0.69104 |
| 1I | 620.42 | 0.183 | HOMO → LUMO | 0.69038 |
| 1Me | 641.62 | 0.1903 | HOMO → LUMO | 0.68641 |
| | | | HOMO → LUMO + 1 | -0.11031 |
| 1OMe | 638.45 | 0.2061 | HOMO → LUMO | 0.68808 |
| | | | HOMO → LUMO + 1 | -0.10008 |
| 2 | 490.01 | 0.2948 | HOMO → LUMO | 0.68485 |
| 3 | 565.88 | 0.1768 | HOMO → LUMO | 0.68756 |
| | | | HOMO → LUMO + 1 | -0.10849 |

1H



1F

1Cl



1Br

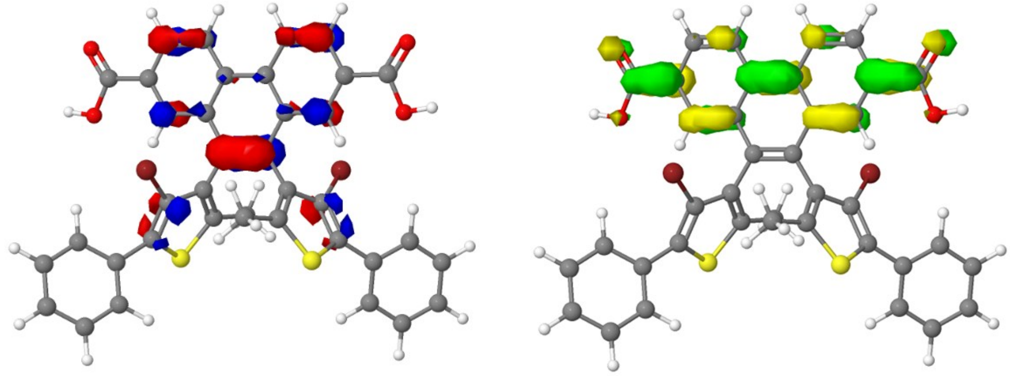
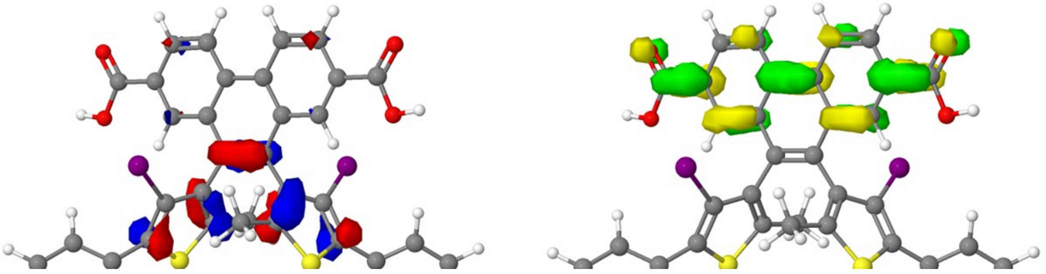
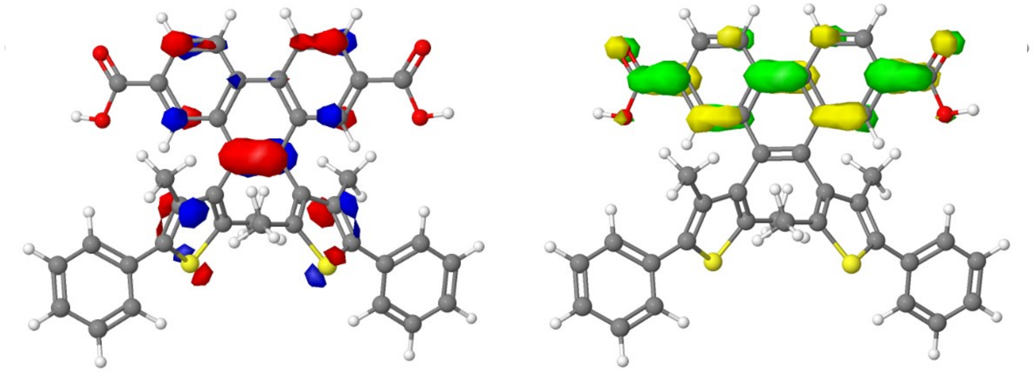


Figure S1a. Isosurfaces of orbitals of open-form molecules involved in lowest energy transition. Left (red/blue): Occupied orbitals, Right (yellow/green): Unoccupied orbitals.

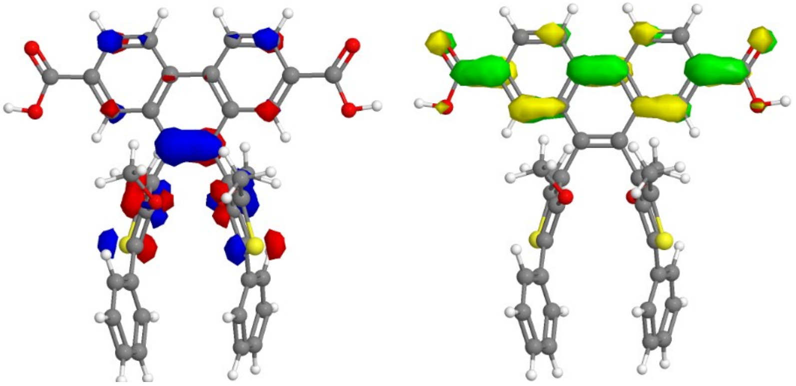
1I





1Me

1OMe



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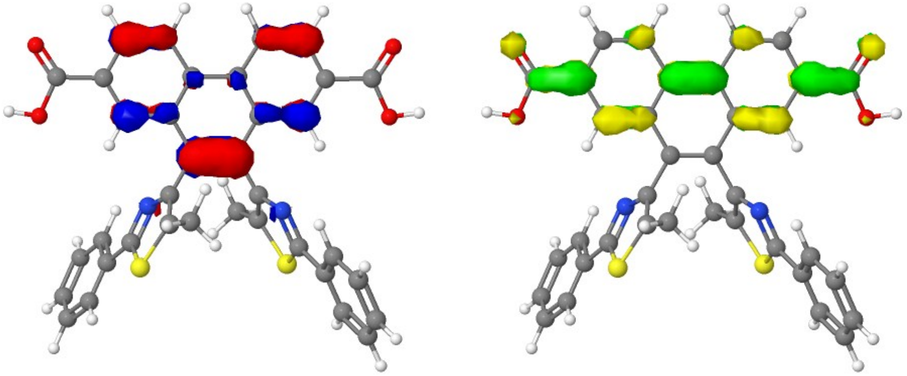


Figure S1b. Isosurfaces of orbitals of open-form molecules involved in lowest energy transition. Left (red/blue): Occupied orbitals, Right (yellow/green): Unoccupied orbitals.

3

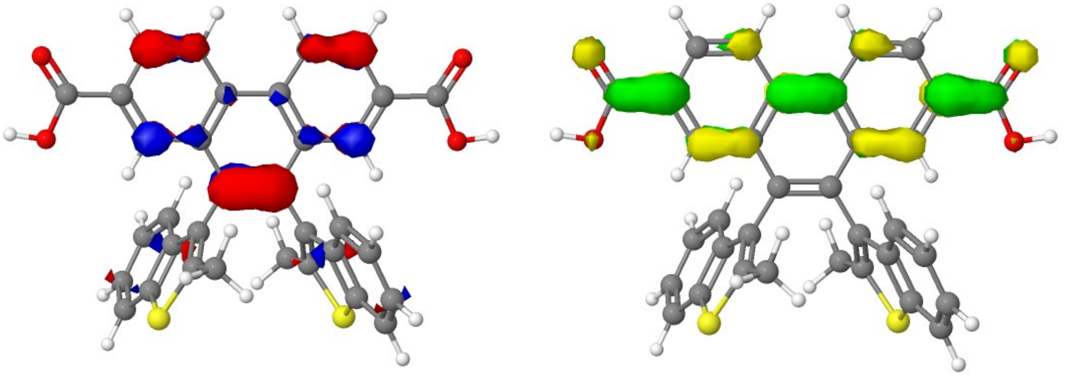


Figure S1c. Isosurfaces of orbitals of open-form molecules involved in lowest energy transition. Left (red/blue): Occupied orbitals, Right (yellow/green): Unoccupied orbitals.

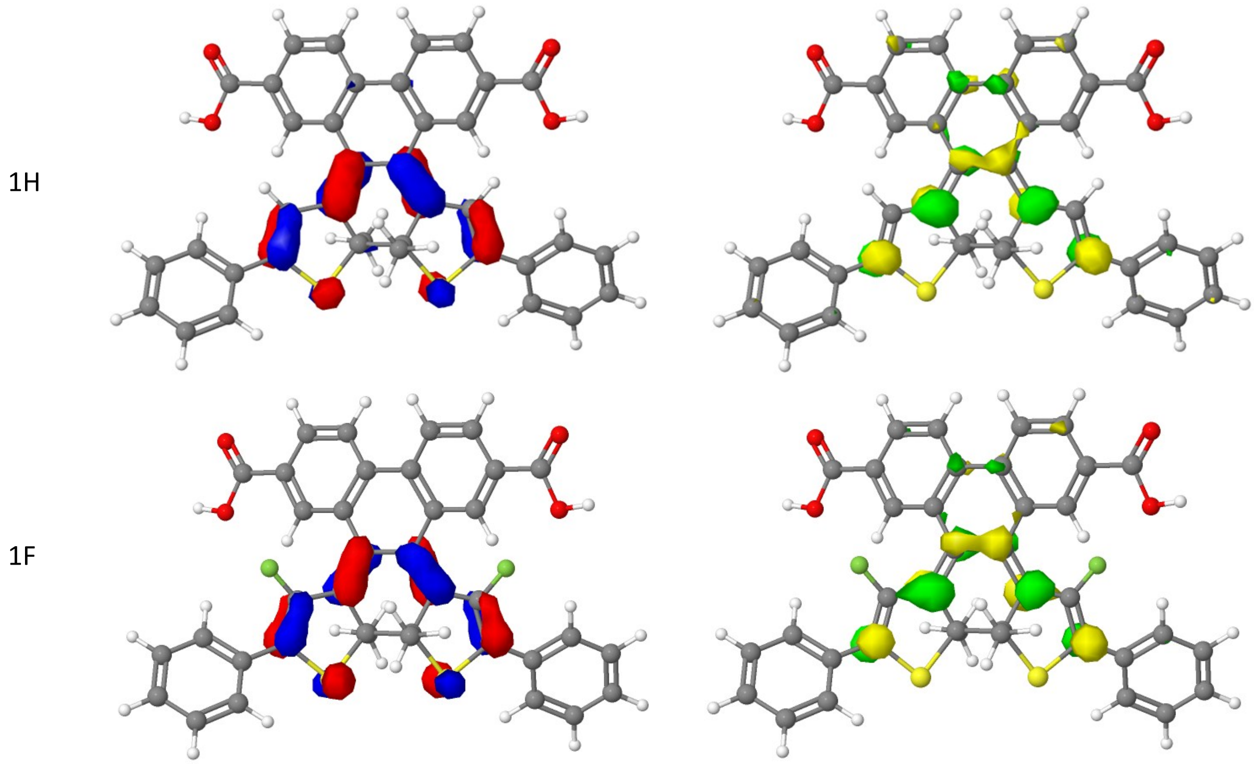


Figure S2a. Isosurfaces of orbitals of closed-form molecules involved in lowest energy transition. Left (red/blue): Occupied orbitals, Right (yellow/green): Unoccupied orbitals.

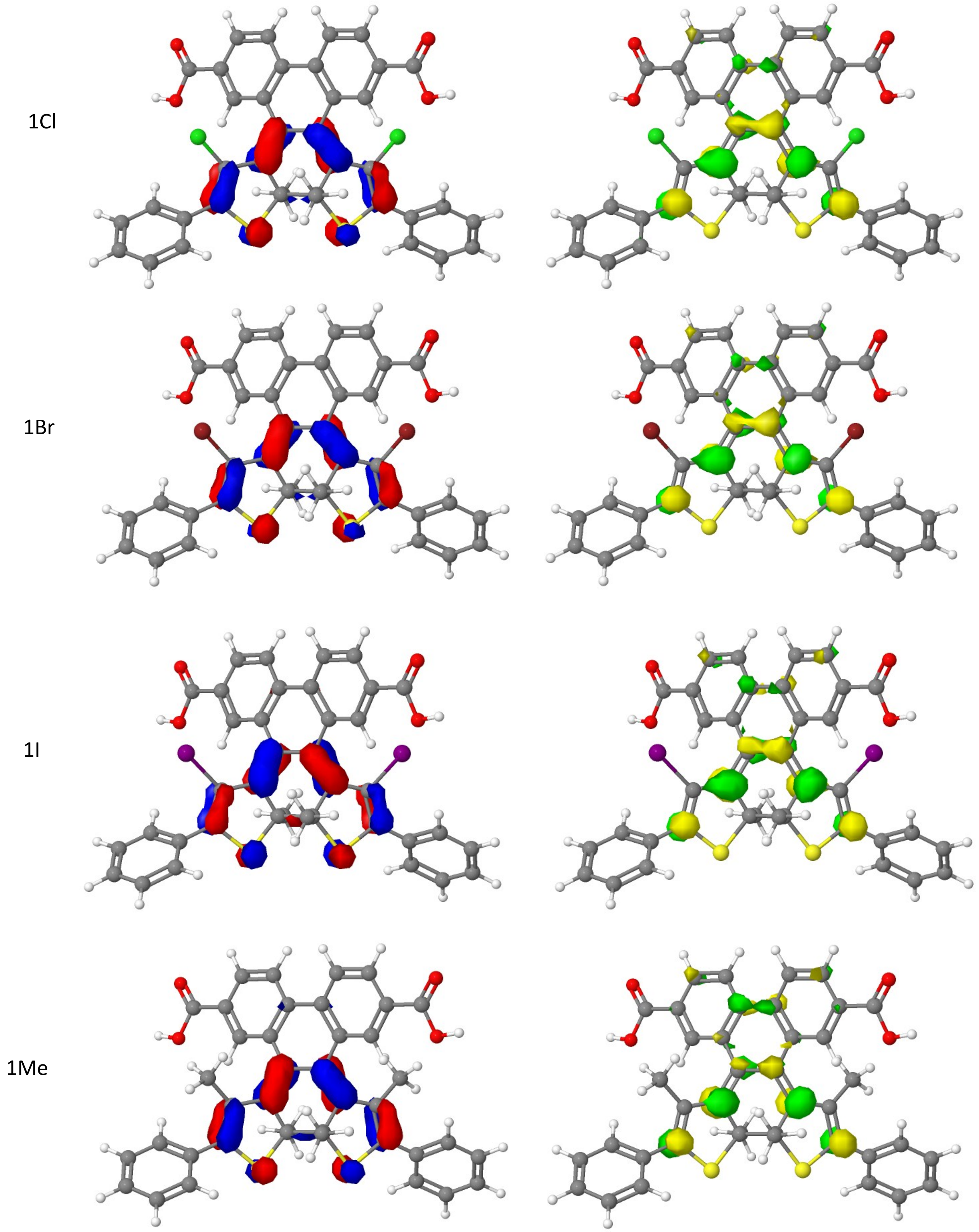
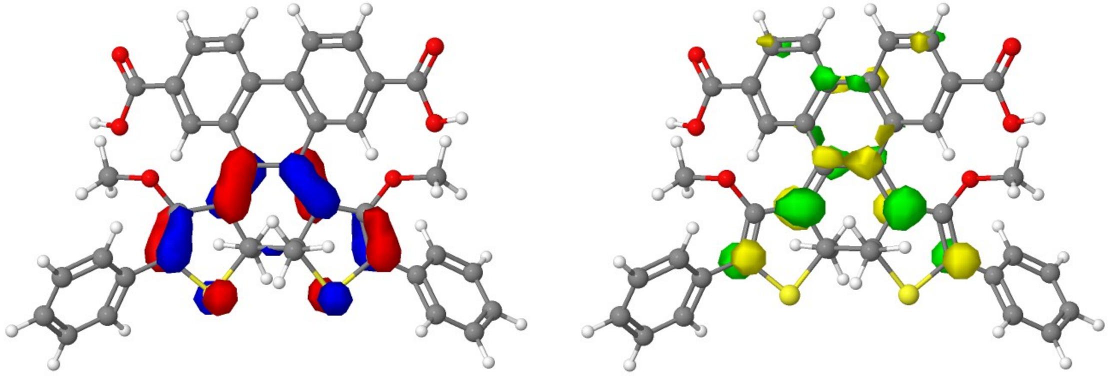


Figure S2b. Isosurfaces of orbitals of closed-form molecules involved in lowest energy transition. Left (red/blue): Occupied orbitals, Right (yellow/green): Unoccupied orbitals.

1OMe



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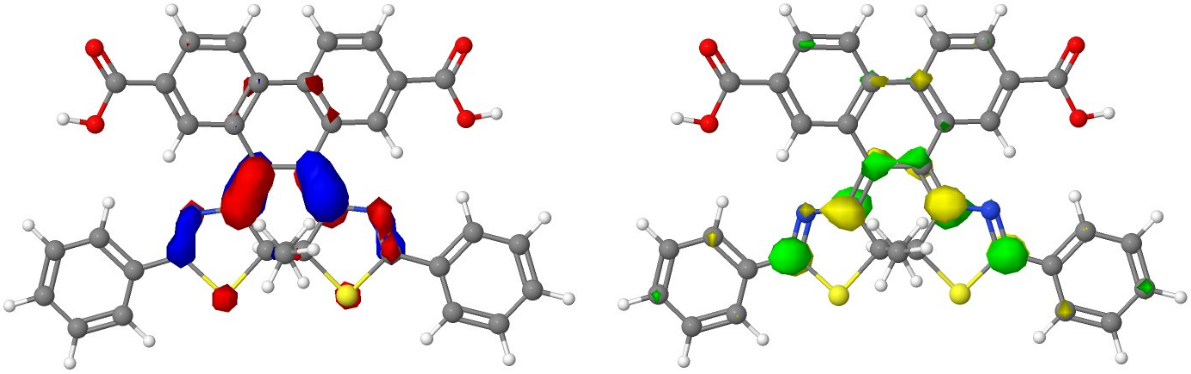

3

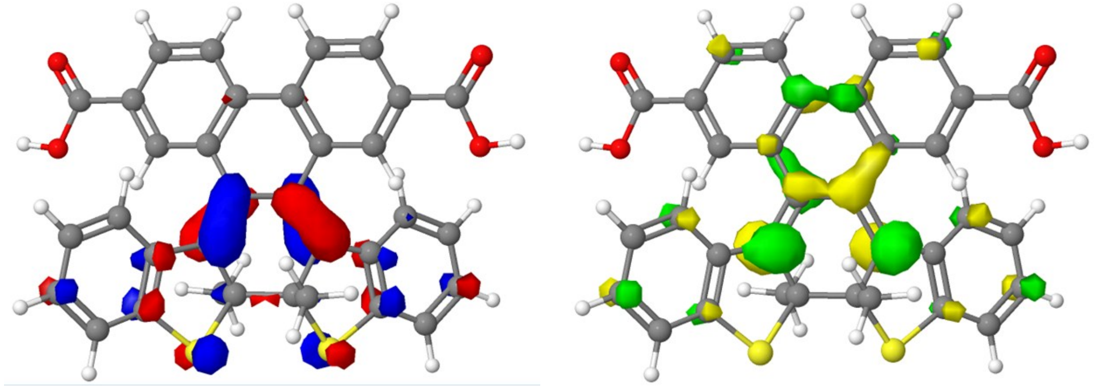

Figure S2c. Isosurfaces of orbitals of closed-form molecules involved in lowest energy transition. Left (red/blue): Occupied orbitals, Right (yellow/green): Unoccupied orbitals.

Table S3. The calculated energies of open and closed forms of all systems, and the energy difference between the two forms.

| Molecule | Open Energy (Hartree) | Closed Energy (Hartree) | ΔE (Hartree) | ΔE (kcal/mol) |
|---|---|---|---|---|
| 1H | -2560.45440742 | -2560.40847009 | 0.04593733 | 28.83 |
| 1F | -2758.86443943 | -2758.80664197 | 0.05779746 | 36.27 |
| 1Cl | -3479.61113779 | -3479.54496100 | 0.06617679 | 41.53 |
| 1Br | -7702.72440358 | -7702.65340612 | 0.07099746 | 44.55 |
| 1I | -2581.99449640 | -2581.92637963 | 0.06811677 | 42.74 |
| 1Me | -2639.07408409 | -2639.01367516 | 0.06040893 | 37.91 |
| 1OMe | -2789.42339159 | -2789.36339165 | 0.05999994 | 37.65 |
| 2 | -2592.54155117 | -2592.51719905 | 0.02435212 | 15.28 |
| 3 | -2405.69613621 | -2405.63964215 | 0.05649406 | 35.45 |

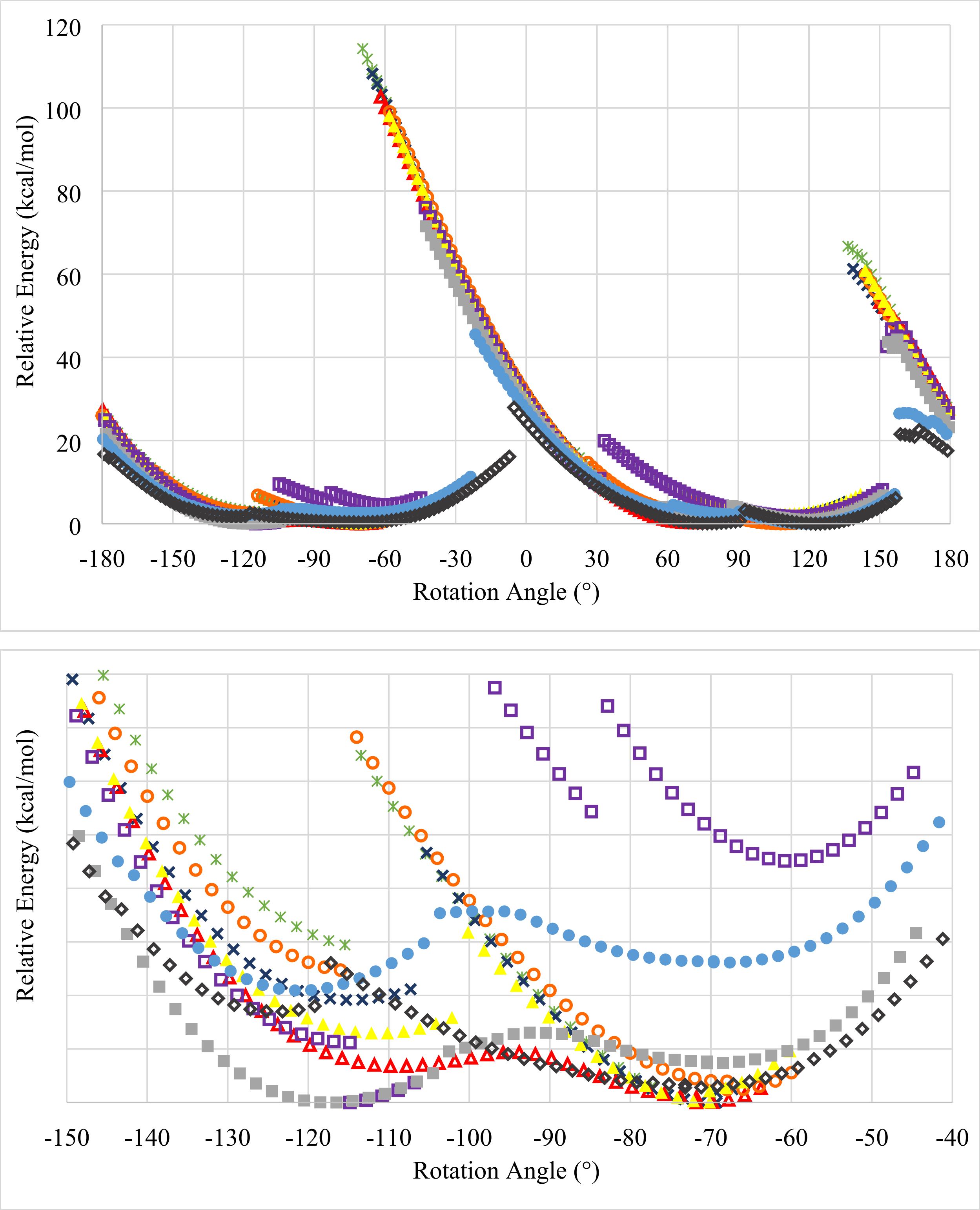

Figure S3a. Reverse-direction rotational potential energy surfaces of all molecules with expanded views of the energy wells. Light-blue circles: **1H**, Light-grey squares: **1F**, Yellow triangles: **1Cl**, Dark-blue X's: **1Br**, Green stars: **1I**, Orange open circles: **1Me**, Violet open squares: **1OMe**, Dark-grey open diamonds: **2**, Red open triangles: **3**.

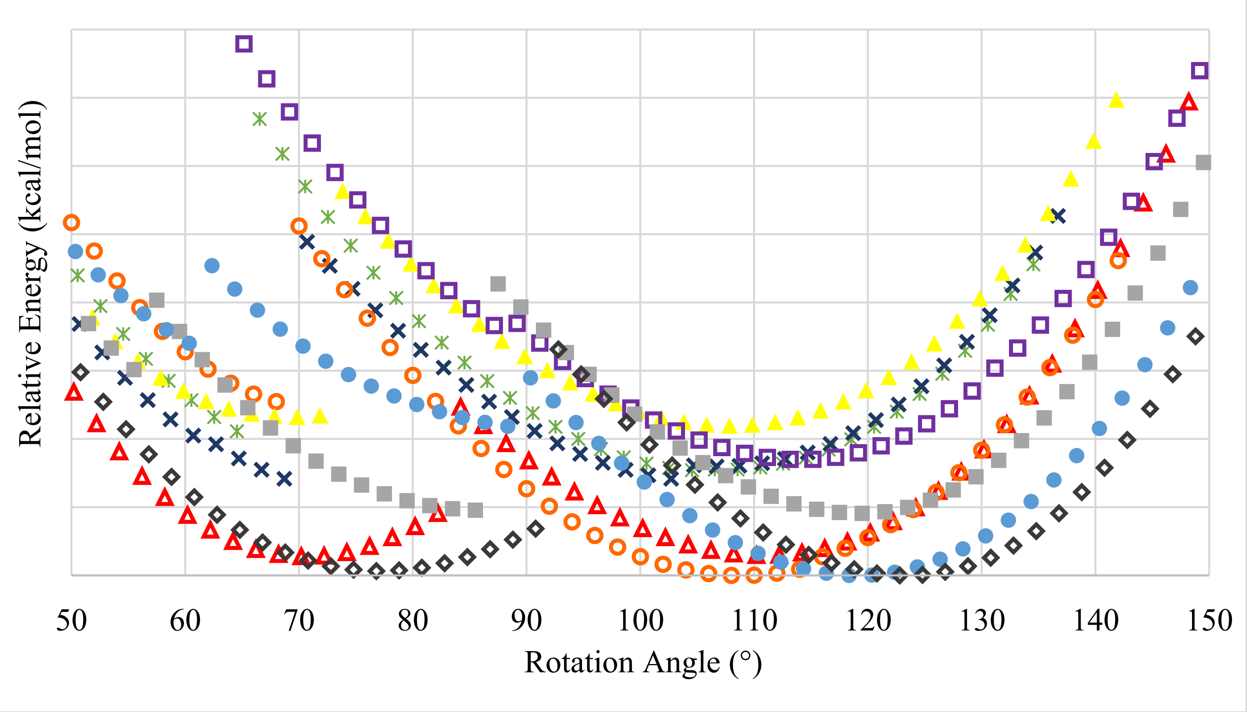

Figure S3b. Reverse-direction rotational potential energy surfaces of all molecules with expanded views of the energy wells. Light-blue circles: **1H**, Light-grey squares: **1F**, Yellow triangles: **1Cl**, Dark-blue X's: **1Br**, Green stars: **1I**, Orange open circles: **1Me**, Violet open squares: **1OMe**, Dark-grey open diamonds: **2**, Red open triangles: **3**.