A luminescent cis iridium(III) complex based on a bis(6,7-dimethoxy-3,4-dihydroisoquinoline) platform featuring an unusual cis orientation of the C^N ligands: from a theoretical approach to a deep red LEEC device

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Materials and methods

All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received.

$^1$H, $^{13}$C and $^{19}$F spectra were acquired on a Bruker DRX (400 MHz) spectrometer. Chemical shifts are given in ppm relative to the internal standard tetramethylsilane (Me$_4$Si) and $J$ values are given in Hz. $^1$H,$^1$H COSY, $^1$H,$^{13}$C HSQC, $^1$H,$^{13}$C HMBC and NOESY experiments were run at 400.1 MHz using standard pulse programs. Mass spectra were recorded in positive and negative ion mode using a 1100 VL LC/MSD Agilent instrument.

Absorption and photoluminescent (PL) spectra were recorded with a UV-vis spectrophotometer (Jasco V-560) and a fluorospectrophotometer (Jasco FP-750). Quantum efficiencies ($\Phi$) were calculated using fluorescein ($\Phi = 0.9$ in a 0.1 M solution of NaOH) as reference.

Analytical and preparative TLC were performed on silica gel plates F254 (0.25 and 0.5 mm, respectively) and were visualized using a UV lamp ($\lambda = 254$ nm) and a fluorescence lamp ($\lambda = 356$ nm). Liquid chromatography was performed on silica gel (60-230 mesh).

The cyclic voltammetry (CV) measurements were performed using a potentiostat/galvanostat model 273A (Princeton Applied Research). Ag/AgCl reference electrode, Pt tip electrode (0.008 mm$^2$
area), and Pt counter electrode were used. For CV measurements, we used an electrolytic solution having standard concentration of 0.1 M di tetrabutylammonium hexafluorophosphate and a scan rate of 50 and 100 mV/s. The system has been previously tested and calibrated using a ferrocene solution in acetonitrile (0.02 M).

The thickness of films was determined with an Taylor Hobson CCI MP profilometer.
Synthetic Procedures

**Synthesis of bis(6,7-dimethoxy-3,4-dihydroisoquinoline).** A reported procedure for the synthesis of the ancillary ligand was followed. In brief, a solution of diethyloxalate (3.66 mL, 27 mmol) in toluene (9 mL) was added to a solution of O,O-dimethyldopamine (1 g, 5.9 mmol) in toluene (50 mL). The mixture was heated to reflux under argon for 5 h and then evaporated under reduced pressure. The crude solid was taken in chloroform and purified by liquid chromatography on silica gel using chloroform as the eluent to give the N1,N2-bis(3,4-dimethoxyphenethyl)oxalamide (1.17 g, 95%, Rf = 0.78 chloroform/methanol 95:5 (v/v)).

\(^1\)H NMR (200 MHz, Acetone-\(d_6\)) \(\delta\) ppm: 6.86 (d, \(J = 2.0\) Hz, 1H), 6.82 (d, \(J = 6.2\) Hz, 1H), 6.76 (dd, \(J = 6.2, 2.0\) Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.49 (t, \(J = 4.0\) Hz, 2H), 2.83 (t, \(J = 4.0\) Hz, 2H).

\(^13\)C NMR (50 MHz, acetone-\(d_6\)) \(\delta\) ppm: 158.7, 150.2, 148.9, 132.3, 121.3, 113.4, 112.7, 63.2, 62.8, 55.9, 41.6.

A solution of the N1,N2-bis(3,4-dimethoxyphenethyl)oxalamide (1.17 g, 2.8 mmol) in 11 mL of a mixture 3:11 (v/v) of ethanol/dichloromethane was treated under stirring with
POCl₃ (3.7 mL, 39 mmol) and kept under reflux. After 5 h, 8.9 mL of light petroleum were added and the mixture was kept at 130 °C overnight. The mixture was filtered and the solid was dissolved in water/methanol (1.7 mL / 50 mL) and treated with K₂CO₃ (350 mg) to adjust the pH to 10 and then extracted with chloroform. The crude solid was purified by liquid chromatography on silica gel using chloroform as eluent to give the pure bis(6,7-dimethoxy-3,4-dihydroisoquinoline) (650 mg, 61%, R₁ = 0.75, chloroform/methanol 95:5 (v/v)). ¹H NMR (400 MHz, CDCl₃) δ ppm: 7.24 (s, 1H), 6.57 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.71 (t, J = 7.6 Hz, 2H), 2.56 (t, J = 7.6, 2H). ¹³C NMR (50 MHz, CDCl₃) δ ppm: 164.4, 151.3, 147.1, 131.2, 118.5, 110.0, 109.8, 55.7, 55.5, 47.2, 24.7. ESI⁺ MS: m/z 381.

Synthesis of [Ir(ppy)₂Cl]₂. For the synthesis of the dichloro-bridged iridium complex was followed the procedure reported by Nonoyama.² In brief, iridium trichloride hydrate (500 mg, 1.67 mmol) was dissolved in a mixture of 32 mL of 2-ethoxyethanol and water 3:1 (v/v) and treated with 480 μL (3.6 mmol) of 2-phenylpyridine under reflux and argon atmosphere. After 24 h the reaction mixture was cooled and filtered on a glass filter frit to obtain a yellow precipitate (644 mg, 72%).
$^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ ppm: 9.30 (d, $J = 8.0$ Hz, 2H), 7.98 (d, $J = 8.0$ Hz, 2H),
7.84 (t, $J = 8.0$ Hz, 2H), 7.60 (d, $J = 8.0$ Hz, 2H), 6.8-6.9 (m, 4H), 6.65 (t, $J = 8.0$ Hz, 2H),
5.92 (d, $J = 8.0$ Hz, 2H).
Figure S1. $^1$H NMR spectrum of $\text{cis-1 (CD}_2\text{Cl}_2$)
Figure S2. $^1$H NMR spectrum of cis-5 (CD$_2$Cl$_2$)
Figure S3. $^1$H NMR spectrum (CD$_2$Cl$_2$, expansion of the aromatic protons region) of a cis-5 enriched fraction obtained from liquid chromatography of the reaction mixture for iridium(III) complex preparation.

- signals diagnostic of cis-5
- signals diagnostic of cis-1
- signals diagnostic of trans-1
Figure S4. $^1$H,$^1$H COSY spectrum (CD$_2$Cl$_2$, expansion of the aromatic protons region) of a cis-5 enriched fraction obtained from liquid chromatography of the reaction mixture for iridium(III) complex preparation.
Figure S5. (a) ESI(+)‐MS spectrum of cis‐1; (b) ESI(−)‐MS spectrum of cis‐1

(a)

(b)
Figure S6. (a) Thermo Gravimetric Analysis (TGA) of cis-1; (b) Differential Scanning Calorimetry (DSC) of cis-1
**Figure S7.** Cyclic voltammogram of *cis*-1 (scan rate = 50 mVs⁻¹).
Figure S8. Three-gaussian best-fit performed on the emission spectrum of cis-1. Experimental emission spectrum registered at 9 K after excitation at 440 nm (bold black line); fitted curve (regular black line); extrapolated single spectral contributions at 2.08 eV (blue line), 1.93 eV (green line) and 1.71 eV (red line).
Figure S9. Normalized PLE spectra obtained at 9 K of the three emission bands E1 (white circle), E2 (yellow square) and E3 (blue circle) of cis-1.
Figure S10. Schematic representation of the main opto-electronic transitions of *cis*-1. Spin-forbidden transitions are highlighted in red.
Figure S11. Characteristic of the LEEC devices #4, #6 and #8
Figure S12. Characteristic of the following LEEC devices: (a) #1; (b) #2; (c) #3; (d) #5
Figure S13. Time-dependence of luminance for the best performing device #7
Computational investigation of structural and spectroscopic properties of iridium complexes

The aim of this investigation is to characterize structural, energetic and spectroscopic features of iridium complexes of 3,3',4,4'-tetrahydro-6,6',7,7'-tetramethoxy-1,1'-biisoquinoline, e.g.:

All calculations were performed with the Gaussian package of programs.\(^3\)

All structures were geometry optimized at the DFT level with a hybrid functional (M06-2X).\(^4\) The 6-31+G(d,p) basis set was used of H, C, N and O atoms; the Stuttgart / Dresden pseudopotential and basis set\(^5,6\) were adopted for the iridium center. For each species, different conformers were explored. In those cases where conformational enantiomers exist, a single enantiomeric series has been examined.

To account for the influence of the solution environment (chloroform), a polarizable continuum medium (PCM) was adopted.\(^7\)\(^-\)\(^10\) In view of the faster convergence, a scaled van der Waals cavity based on universal force field (UFF) radii\(^11\) was used, and polarization charges were modeled by spherical Gaussian functions.\(^12,13\) Vibrational-rotational contributions to the free energy were also computed.

UV-Vis spectra of the main species were computed in solution using the time-dependent density functional theory (TD-DFT) approach,\(^14\)\(^-\)\(^18\) with the same functional / basis set / pseudopotential combination. For the purpose of comparison, selected TD-DFT calculations were also performed using the PBE0,\(^19\) CAM-B3LYP\(^20\) or the LC-\(\omega\)PBE\(^21\) functional. To produce graphs, transitions below 5.6 eV were selected, and an arbitrary Gaussian line width of 0.25 eV was imposed; the spectra were finally converted to a wavelength scale. The non-equilibrium linear response formulation of the PCM was adopted for TD-DFT calculations; a state-specific approach\(^12,23\) was employed to evaluate the energy of the first triplet state at the equilibrium geometry of the ground-state singlet, or vice-versa the energy of the ground-state singlet at the equilibrium geometry of the first triplet.
Part 1: Parent compound

![Parent Compound Image]

Table S1. Structural exploration of alternative isomers / conformers of the parent compound (monocation, singlet). In parentheses relative energies (kcal mol\(^{-1}\)) referred to the most stable form (in bold) identified at the specified level.

| #   | Isomer / Conformer a | Symmetry | \(E_{PCM} / \text{Ha}\) b | \(H_{PCM,RRHO} / \text{Ha}\) | \(G_{PCM,RRHO} / \text{Ha}\) |
|-----|----------------------|----------|---------------------------|-----------------------------|-----------------------------|
| apical_apical/.../conf1.symm | apical, apical, conf1 | C\(_2\) | - 1866.09674 8 (0.0) | - 1865.43333 4 (0.0) | - 1865.53593 3 (0.0) |
| apical_apical/.../conf2.symm | apical, apical, conf2 | C\(_2\) | - 1866.09405 5 (1.7) | - 1865.43058 1 (1.7) | - 1865.53284 9 (1.9) |
| apical_equatorial/.../conf1 | apical, equatorial, conf1 | C\(_1\) | - 1866.09481 6 (1.2) | - 1865.43115 9 (1.4) | - 1865.53497 5 (0.6) |
| apical_equatorial/.../conf2 | apical, equatorial, conf2 | C\(_1\) | - 1866.09361 6 (2.0) | - 1865.43002 0 (2.1) | - 1865.53588 7 (0.0) |
| equatorial_equatorial/.../conf1.sym | equatorial, equatorial, | C\(_2\) | - 1866.07920 | - 1865.41585 | - 1865.52104 |
| m | conf1 | 0 (11.0) | 6 (11.0) | 9 (9.3) |
|---|---|---|---|---|
| `equatorial_equatorial/.../conf2.sym` | equatorial, equatorial, conf2 | $C_2$ | $-1866.079648$ (10.7) | $-1865.415914$ (10.9) | $-1865.517635$ (11.5) |

[a] For chiral structures, only one enantiomer is listed.

[b] Electronic energy.
Figure S14. UV-Vis spectra computed at the TD-M062X level for several isomers / conformers of the parent compound (monocation, singlet).
Figure S15. UV-Vis spectra computed with several different functionals, for two conformers of the apical, apical isomer of the parent compound (monocation, singlet).

Parent compound, apical, apical isomer
TD-DFT / 6-31+G(d,p) / PCM (chloroform) // M062X / 6-31+G(d,p) / PCM (chloroform)
Part 2: Model 1

![Image of model 1](image-url)

Table S2. Structural exploration of alternative isomers / conformers of model 1 (monocation, singlet). In parentheses relative energies (kcal mol\(^{-1}\)) referred to the most stable form (in bold) identified at the specified level.

| #    | Isomer / Conformer | Symmetry | \(E_{PCM} / \text{Ha}\)^b | \(H_{PCM,RRHO} / \text{Ha}\) | \(G_{PCM,RRHO} / \text{Ha}\) |
|------|--------------------|----------|---------------------------|-----------------------------|-----------------------------|
| 1    | apical_apical/.../conf1.smm | apical, apical, conf1 | \(C_2\) | - 1251.69603 2 (0.0) | - 1251.23241 2 (0.0) | - 1251.31064 8 (0.2) |
| 2    | apical_apical/.../conf2.smm | apical, apical, conf2 | \(C_2\) | - 1251.69577 0 (0.2) | - 1251.23246 2 (0.0) | - 1251.31097 3 (0.0) |
| 3    | apical_apical/.../conf1 | apical, equatorial, conf1 | \(C_1\) | - 1251.69344 8 (1.6) | - 1251.23015 0 (1.5) | - 1251.30926 9 (1.1) |
| 4    | apical_apical/.../conf2 | apical, equatorial, conf2 | \(C_1\) | - 1251.69359 2 (1.5) | - 1251.23054 7 (1.2) | - 1251.31011 2 (0.5) |
| 5    | equatorial_equatorial/.../conf1.smm | apical, apical, conf1 | \(C_2\) | - 1251.67804 0 (11.3) | - 1251.21459 8 (11.2) | - 1251.29188 6 (12.0) |
| 6    | equatorial_equatorial/.../conf2.smm | apical, apical, conf2 | \(C_2\) | - 1251.67836 2 (11.1) | - 1251.21526 2 (10.8) | - 1251.29317 1 (11.2) |

[a] For chiral structures, only one enantiomer is listed.

[b] Electronic energy.
Figure S16. UV-Vis spectra computed at the TD-M062X level for several isomers / conformers of model 1 (monocation, singlet).
### Table S3. Structural exploration of alternative conformers of the apical, apical isomer of model 2 (monocation, singlet). In parentheses relative energies (kcal mol\(^{-1}\)) referred to the most stable form (in bold) identified at the specified level.

| #                  | Isomer / Conformer\(^a\) | Symmetry | \(E_{\text{PCM}} / \text{Ha}\)\(^b\) | \(H_{\text{PCM,RHO}} / \text{Ha}\) | \(G_{\text{PCM,RHO}} / \text{Ha}\) |
|--------------------|--------------------------|----------|-------------------------------------|----------------------------------|---------------------------------|
| apical_apical/.../conf1_1.symm | apical, apical, conf1_1 | \(C_2\)  | -1709.619821 (0.8)                  | -1709.014232 (0.8)              | -1709.117151 (1.4)             |
| apical_apical/.../conf1_2.symm | apical, apical, conf1_2 | \(C_2\)  | -1709.611761 (5.9)                  | -1709.006734 (5.5)              | -1709.112059 (4.6)             |
| apical_apical/.../conf1_3.symm | apical, apical, conf1_1 | \(C_2\)  | -1709.610939 (6.4)                  | -1709.005565 (6.2)              | -1709.108790 (6.7)             |
| apical_apical/.../conf1_4.symm | apical, apical, conf1_2 | \(C_2\)  | -1709.617614 (2.2)                  | -1709.012236 (2.1)              | -1709.113375 (3.8)             |
| apical_apical/.../conf1_5 | apical, apical, conf1_1 | \(C_2\)  | -1709.621151 (0.0)                  | -1709.015523 (0.0)              | -1709.118781 (0.4)             |
| apical_apical/.../conf2_1.symm | apical, apical, conf1_2 | \(C_2\)  | -1709.619438 (1.1)                  | -1709.014034 (0.9)              | -1709.117115 (1.5)             |
| apical_apical/.../conf2_3.symm | apical, apical, conf1_2 | \(C_2\)  | -1709.619939 (0.8)                  | -1709.014350 (0.7)              | -1709.115157 (2.7)             |
| apical_apical/.../conf2_5 | apical, apical, conf1_2 | \(C_2\)  | -1709.620634 (0.3)                  | -1709.015211 (0.2)              | -1709.119426 (0.0)             |

\(^a\) For chiral structures, only one enantiomer is listed.

\(^b\) Electronic energy.
Figure S17. UV-Vis spectra computed at the TD-M062X level for several conformers of the apical, apical isomer of model 2 (monocation, singlet).
**Part 4: Tetramethoxy-substituted compound**

![Chemical structure image](Image)

**Table S4.** Structural exploration of alternative isomers / conformers of the tetramethoxy-substituted compound (monocation, singlet). In parentheses relative energies (kcal mol\(^{-1}\)) referred to the most stable form (in bold) identified at the specified level.

| #     | Isomer / Conformer\(^{a}\)          | Symmetry | \(E_{\text{PCM}} / \text{Ha}\)\(^{b}\) | \(H_{\text{PCM,RRHO}} / \text{Ha}\) | \(G_{\text{PCM,RRHO}} / \text{Ha}\) |
|-------|-----------------------------------|----------|----------------------------------|----------------------------------|----------------------------------|
| apical_apical/.../conf1_5 | apical, apical, conf1_5           | \(C_1\)  | -2324.022163 (0.0)               | -2323.216199 (0.0)               | -2323.343360 (0.0)               |
| apical_apical/.../conf2_5 | apical, apical, conf2_5           | \(C_1\)  | -2324.019387 (1.7)               | -2323.213914 (1.4)               | -2323.342310 (0.7)               |
| apical_equatorial/.../conf1_5 | apical, equatorial, conf1_5      | \(C_1\)  | -2324.019532 (1.7)               | -2323.213177 (1.9)               | -2323.339923 (2.2)               |
| apical_equatorial/.../conf1_6 | apical, equatorial, conf1_6      | \(C_1\)  | -2324.019677 (1.6)               | -2323.213547 (1.7)               | -2323.342237 (0.7)               |
| apical_equatorial/.../conf2_5 | equatorial, equatorial, conf2_5  | \(C_1\)  | -2324.018434 (2.3)               | -2323.212823 (2.1)               | -2323.340840 (1.6)               |
| apical_equatorial/.../conf2_6 | equatorial, equatorial, conf2_6  | \(C_1\)  | -2324.018804 (2.1)               | -2323.212947 (2.0)               | -2323.339769 (2.3)               |

\(\text{[a]}\) For chiral structures, only one enantiomer is listed.

\(\text{[b]}\) Electronic energy.
**Table S5.** Computed [TD-M062X / 6-31+G(d,p) /PCM] high-wavelength (\( \lambda > 300 \) nm) spin-allowed (singlet – singlet) electronic transitions in chloroform.

| \( \lambda / \text{nm}^a \) | \( f \) | Contribution (expansion coefficient) | \( \lambda / \text{nm}^a \) | \( f \) | Contribution (expansion coefficient) | \( \lambda / \text{nm}^a \) | \( f \) | Contribution (expansion coefficient) |
|-----------------------------|---------|--------------------------------------|-----------------------------|---------|--------------------------------------|-----------------------------|---------|--------------------------------------|
| 404.4 [3.07]               | 0.00    | 190 → 191 (0.67)                     | 406.2 [3.05]                | 0.00    | 190 → 191 (0.68)                     | 407.1 [3.05]                | 0.03    | 179 → 191 (0.14)                     |
|                             |         | 185 → 191 (-0.11)                    |                            |         | 188 → 191 (0.10)                     |                            |         | 189 → 191 (0.12)                     |
|                             |         | 190 → 191 (0.63)                     |                            |         |                                      |                            |         |                                      |
| 344.9 0.46                  |         | 182 → 191 (-0.12)                    | 350.6 0.42                 | 182 → 191 (0.11)                    | 379.3 0.10                | 180 → 191 (0.11)                    |
|                             |         | 184 → 191 (-0.10)                    |                            | 184 → 191 (-0.10)                   |                            | 181 → 191 (-0.14)                 |
|                             |         | 188 → 191 (-0.11)                    |                            | 188 → 191 (0.32)                    |                            | 186 → 191 (0.14)                 |
|                             |         | 189 → 191 (0.65)                     |                            | 189 → 191 (0.58)                    |                            | 189 → 191 (0.63)                 |
|                             |         | 190 → 193 (-0.11)                    |                            |                                      |                            | 190 → 191 (-0.15)               |
| 340.6 0.08                  |         | 183 → 191 (-0.27)                    | 348.0 0.11                 | 183 → 191 (0.25)                    | 357.6 0.33                | 183 → 191 (0.15)                    |
|                             |         | 186 → 191 (-0.12)                    |                            | 187 → 191 (0.50)                    |                            | 184 → 191 (-0.11)                |
|                             |         | 187 → 191 (0.61)                     |                            | 188 → 191 (0.35)                    |                            | 188 → 191 (0.63)                 |
|                             |         |                                      |                            | 189 → 191 (-0.17)                   |                            | 190 → 191 (-0.12)                |
| 329.6 0.17                  |         | 188 → 193 (-0.17)                    | 328.9 0.17                 | 188 → 193 (-0.11)                   | 326.4 0.16                | 185 → 191 (0.14)                    |
|                             |         | 190 → 191 (-0.11)                    |                            | 189 → 193 (0.11)                    |                            | 187 → 191 (0.65)                 |
|                             |         | 190 → 192 (0.64)                     |                            | 190 → 192 (0.65)                    |                            |                                      |
| 318.7 0.05                  |         | 188 → 191 (-0.12)                    | 316.4 0.02                 | 187 → 192 (0.13)                    | 314.7 0.09                | 187 → 191 (-0.11)                    |
|                             |         | 188 → 192 (0.64)                     |                            | 188 → 192 (0.65)                    |                            |                                      |
| 188 → 192 (0.22) | 189 → 191 (0.10) | 190 → 193 (0.62) | 187 → 192 (0.11) | 187 → 193 (0.10) | 190 → 192 (0.47) | 190 → 193 (0.43) |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 189 → 191 (0.14) | 189 → 192 (0.16) | 190 → 193 (0.61) |
| 189 → 191 (0.14) | 189 → 192 (0.16) | 190 → 193 (0.61) |
| 189 → 191 (0.14) | 189 → 192 (0.16) | 190 → 193 (0.61) |
| 189 → 191 (0.14) | 189 → 192 (0.16) | 190 → 193 (0.61) |
| 189 → 191 (0.14) | 189 → 192 (0.16) | 190 → 193 (0.61) |
| 189 → 191 (0.14) | 189 → 192 (0.16) | 190 → 193 (0.61) |
| 189 → 191 (0.14) | 189 → 192 (0.16) | 190 → 193 (0.61) |
| 189 → 191 (0.14) | 189 → 192 (0.16) | 190 → 193 (0.61) |

| 183 → 191 (0.53) | 186 → 191 (0.24) | 187 → 191 (0.28) | 189 → 194 (0.12) | 187 → 192 (0.11) | 187 → 193 (0.10) | 190 → 192 (0.47) | 190 → 193 (0.43) |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 183 → 191 (0.57) | 186 → 191 (0.25) | 187 → 191 (0.19) | 188 → 191 (0.17) |
| 183 → 191 (0.57) | 186 → 191 (0.25) | 187 → 191 (0.19) | 188 → 191 (0.17) |
| 183 → 191 (0.57) | 186 → 191 (0.25) | 187 → 191 (0.19) | 188 → 191 (0.17) |
| 183 → 191 (0.57) | 186 → 191 (0.25) | 187 → 191 (0.19) | 188 → 191 (0.17) |

| 180 → 191 (0.26) | 184 → 191 (0.19) | 185 → 191 (0.11) | 187 → 191 (0.36) |
|------------------|------------------|------------------|------------------|
| 180 → 191 (0.26) | 184 → 191 (0.19) | 185 → 191 (0.11) | 187 → 191 (0.36) |
| 180 → 191 (0.26) | 184 → 191 (0.19) | 185 → 191 (0.11) | 187 → 191 (0.36) |
| 180 → 191 (0.26) | 184 → 191 (0.19) | 185 → 191 (0.11) | 187 → 191 (0.36) |
| 180 → 191 (0.26) | 184 → 191 (0.19) | 185 → 191 (0.11) | 187 → 191 (0.36) |

| 179 → 191 (0.14) | 183 → 191 (0.11) | 185 → 191 (0.12) | 188 → 191 (0.13) |
|------------------|------------------|------------------|------------------|
| 179 → 191 (0.14) | 183 → 191 (0.11) | 185 → 191 (0.12) | 188 → 191 (0.13) |
| 179 → 191 (0.14) | 183 → 191 (0.11) | 185 → 191 (0.12) | 188 → 191 (0.13) |
| 179 → 191 (0.14) | 183 → 191 (0.11) | 185 → 191 (0.12) | 188 → 191 (0.13) |
| 179 → 191 (0.14) | 183 → 191 (0.11) | 185 → 191 (0.12) | 188 → 191 (0.13) |

| 180 → 191 (0.11) | 181 → 191 (0.13) | 186 → 191 (0.15) | 180 → 191 (0.12) | 181 → 191 (0.15) | 186 → 191 (0.15) |
|------------------|------------------|------------------|------------------|------------------|------------------|
| 385.3            | 0.00             |                  | 384.9            | 0.00             |                  |
| 385.3            | 0.00             |                  | 384.9            | 0.00             |                  |
| 385.3            | 0.00             |                  | 384.9            | 0.00             |                  |
| 385.3            | 0.00             |                  | 384.9            | 0.00             |                  |

**Note:** The values are rounded to two decimal places for simplicity.
| 360.4 | 0.32 | 183 → 191 (0.15) | 184 → 191 (0.10) | 188 → 191 (0.63) | 190 → 191 (0.13) | 368.1 | 0.40 | 183 → 191 (0.16) | 184 → 191 (0.11) | 188 → 191 (0.63) | 190 → 191 (0.17) | 365.8 | 0.41 | 183 → 191 (0.16) | 184 → 191 (0.12) | 188 → 191 (0.63) | 190 → 191 (0.16) |
|-------|------|-----------------|-----------------|-----------------|-----------------|-------|------|-----------------|-----------------|-----------------|-----------------|-------|------|-----------------|-----------------|-----------------|-----------------|
| 325.4 | 0.17 | 185 → 191 (0.15) | 187 → 191 (0.64) | 190 → 192 (0.12) | 329.6 | 0.13 | 185 → 191 (0.11) | 186 → 191 (0.15) | 187 → 191 (0.65) | 331.5 | 0.12 | 185 → 191 (0.11) | 186 → 191 (0.13) | 187 → 191 (0.65) |
| 315.0 | 0.10 | 187 → 191 (-0.13) | 187 → 192 (0.12) | 190 → 192 (0.51) | 190 → 193 (-0.37) | 312.1 | 0.10 | 190 → 192 (0.51) | 190 → 193 (0.42) | 312.4 | 0.11 | 187 → 192 (-0.11) | 190 → 192 (0.54) | 190 → 193 (-0.37) |
| 304.2 | 0.17 | 189 → 192 (0.44) | 189 → 193 (0.36) | 190 → 192 (-0.22) | 190 → 193 (-0.27) | 303.5 | 0.14 | 183 → 191 (-0.18) | 184 → 191 (-0.11) | 189 → 192 (0.48) | 189 → 193 (-0.35) | 190 → 192 (-0.14) | 190 → 193 (0.15) | 302.7 | 0.14 | 183 → 191 (-0.17) | 184 → 191 (-0.12) | 189 → 192 (0.44) | 189 → 193 (0.39) | 190 → 192 (-0.14) | 190 → 193 (-0.18) |
|       |      | 300.8 | 0.07 | 183 → 191 (0.39) | 184 → 191 (0.37) | 186 → 191 (-0.18) |       |      |
Table S6. Computed [TD-M062X / 6-31+G(d,p) /PCM] high-wavelength (λ > 350 nm) spin-forbidden (singlet – triplet) electronic transitions in chloroform.

| λ/ nm² | Contribution (expansion coefficient) | λ/ nm² | Contribution (expansion coefficient) | λ/ nm² | Contribution (expansion coefficient) |
|--------|--------------------------------------|--------|--------------------------------------|--------|--------------------------------------|
|        | apical, apical, conf1_5              |        | apical, apical, conf2_5              |        | apical, equatorial, conf1_5         |
| 463.6  | 173 → 191 (-0.14)                    | 173 → 191 (-0.18) | 173 → 191 (0.16) |
| [2.67] | 174 → 191 (0.15)                     | 174 → 191 (0.14) | 179 → 191 (0.12) |
|        | 187 → 191 (0.51)                     | 179 → 191 (0.10) | 183 → 191 (0.15) |
|        | 189 → 194 (-0.22)                    | 183 → 191 (0.11) | 187 → 191 (0.34) |
|        | 190 → 191 (0.27)                     | 187 → 191 (0.39) | 188 → 191 (0.34) |
| 438.4  | 187 → 191 (0.10)                     | 186 → 191 (0.27) | 187 → 191 (-0.12) |
|        | 187 → 194 (-0.26)                    | 187 → 194 (0.18) | 187 → 191 (0.43) |
|        | 188 → 191 (-0.12)                    | 188 → 191 (0.15) | 188 → 194 (-0.11) |
|        | 189 → 191 (0.59)                     | 188 → 194 (0.17) | 189 → 191 (0.23) |
| 410.7  | 173 → 191 (0.12)                     | 189 → 191 (0.53) | 190 → 191 (-0.38) |
|        | 187 → 191 (-0.22)                    | 190 → 191 (0.64) |                           |

[a] In parentheses transition energies in eV.
[b] HOMO is MO #190.
|     | 188 → 193 (-0.14) | 190 → 191 (0.53) | 190 → 192 (0.26) | 187 → 191 (-0.24) | 189 → 191 (0.42) | 190 → 191 (0.26) | 190 → 192 (-0.17) |
|-----|-------------------|-----------------|-----------------|-------------------|-----------------|-----------------|-----------------|
| 383.0 | 186 → 193 (-0.20) | 188 → 192 (-0.39) | 189 → 192 (-0.13) | 190 → 193 (0.45) | 186 → 192 (0.20) | 187 → 193 (0.18) | 188 → 193 (-0.20) |
|      | 382.9             |                 |                 |                   | 189 → 193 (0.20) | 190 → 191 (-0.17) | 190 → 192 (0.50) |
| 384.0 | 186 → 191 (0.15)  | 187 → 191 (0.23) | 187 → 193 (-0.10) | 187 → 194 (0.13) | 188 → 191 (-0.21) | 189 → 191 (0.33) | 189 → 192 (-0.13) |
|      |                   |                 |                 |                   | 190 → 191 (-0.14) | 190 → 192 (0.21) | 190 → 193 (0.22) |
| 381.2 | 186 → 192 (-0.20) | 188 → 193 (-0.30) | 189 → 193 (-0.11) | 190 → 191 (-0.28) | 190 → 192 (0.44) | 186 → 193 (0.20) | 187 → 192 (0.21) |
|      | 381.6             |                 |                 |                   | 188 → 192 (-0.25) | 189 → 192 (0.24) | 190 → 193 (0.45) |
| 377.7 | 185 → 191 (-0.11) | 185 → 192 (0.11) | 187 → 191 (-0.25) | 187 → 192 (-0.15) | 187 → 193 (-0.12) | 187 → 194 (-0.13) | 188 → 191 (0.12) |
|      |                   |                 |                 |                   | 190 → 191 (0.24) | 190 → 192 (0.30) | 190 → 193 (0.28) |
| 373.1 | 185 → 192 (-0.10) | 186 → 192 (0.21) | 186 → 193 (-0.19) | 189 → 191 (-0.15) | 189 → 192 (-0.35) | 186 → 192 (0.21) | 186 → 193 (-0.19) |
|      |                   |                 |                 |                   |                    |                 |                 |
|        |                   |                   |                   |
|--------|-------------------|-------------------|-------------------|
|        | apical, equatorial, conf1_6 | apical, equatorial, conf2_5 | apical, equatorial, conf2_6 |
|        | 173 → 191 (-0.16)   | 173 → 191 (-0.16) | 173 → 191 (-0.16) |
| 492.9  | 179 → 191 (0.11)    | 183 → 191 (0.18)  | 183 → 191 (0.18)  |
|        | 183 → 191 (0.16)   | 187 → 191 (-0.30) | 187 → 191 (-0.30) |
| [2.52] | 187 → 191 (0.29)   | 188 → 191 (0.47)  | 188 → 191 (0.47)  |
|        | 188 → 191 (0.41)   | 188 → 194 (-0.18) | 188 → 194 (-0.18) |
|        | 188 → 194 (0.16)   | 188 → 194 (0.47)  | 188 → 194 (0.47)  |
|        | 189 → 191 (0.10)   | 190 → 191 (-0.19) | 190 → 191 (-0.19) |
|        | 190 → 191 (-0.30)  |                   |                   |
|        | 494.4 [2.51]       |                   |                   |
|        |                   |                   |                   |
|        | 179 → 191 (-0.10)  | 179 → 191 (-0.12) | 179 → 191 (-0.12) |
| 466.7  | 187 → 191 (-0.19)  | 187 → 191 (0.25)  | 187 → 191 (0.25)  |
|        | 187 → 194 (0.16)   | 187 → 194 (0.17)  | 187 → 194 (0.17)  |
|        | 188 → 191 (0.38)   | 188 → 191 (0.37)  | 188 → 191 (0.37)  |
|        | 188 → 194 (0.11)   | 189 → 191 (0.10)  | 189 → 191 (0.10)  |
|        | 189 → 191 (0.21)   | 190 → 191 (0.43)  | 190 → 191 (0.43)  |
|        | 190 → 191 (0.42)   |                   |                   |
|        | 464.0 [2.51]       |                   |                   |
|        |                   |                   |                   |
|        | 181 → 191 (0.16)   | 181 → 191 (0.12)  | 181 → 191 (0.12)  |
| 392.6  | 187 → 191 (-0.20)  | 185 → 191 (-0.13) | 185 → 191 (-0.13) |
|        | 189 → 191 (0.46)   | 187 → 191 (0.21)  | 187 → 191 (0.21)  |
|        | 190 → 191 (-0.24)  | 187 → 194 (0.10)  | 187 → 194 (0.10)  |
|        | 190 → 192 (-0.16)  | 189 → 191 (0.47)  | 189 → 191 (0.47)  |
|        |                   | 190 → 191 (-0.32) | 190 → 191 (-0.32) |
|        | 400.1 [2.51]       |                   |                   |
|        |                   |                   |                   |
|        | 185 → 191 (0.12)   | 181 → 191 (0.12)  | 181 → 191 (0.12)  |
| 384.7  | 186 → 191 (0.13)   | 185 → 191 (-0.13) | 185 → 191 (-0.13) |
|        | 187 → 191 (0.28)   | 187 → 191 (0.21)  | 187 → 191 (0.21)  |
|        |                   | 187 → 194 (0.10)  | 187 → 194 (0.10)  |
|        | 388.9 [2.51]       | 189 → 191 (0.47)  | 189 → 191 (0.47)  |
|        |                   | 190 → 191 (-0.32) | 190 → 191 (-0.32) |
|        | 388.6 [2.51]       |                   |                   |
|        |                   |                   |                   |
| Transition | Energy (eV) | Transition | Energy (eV) | Transition | Energy (eV) |
|------------|------------|------------|------------|------------|------------|
| 187 → 194  | -0.15      | 187 → 194  | -0.14      | 187 → 194  | -0.13      |
| 188 → 191  | -0.17      | 188 → 191  | -0.12      | 188 → 191  | -0.12      |
| 189 → 191  | 0.30       | 189 → 191  | 0.38       | 189 → 191  | 0.40       |
| 189 → 192  | 0.11       | 190 → 191  | 0.24       | 190 → 191  | 0.22       |
| 190 → 191  | 0.16       | 190 → 192  | -0.14      | 190 → 192  | -0.14      |
| 190 → 192  | 0.25       | 190 → 193  | -0.15      | 190 → 193  | 0.14       |
| 190 → 193  | -0.20      | 187 → 194  | -0.14      | 187 → 194  | -0.13      |
| 185 → 191  | -0.12      | 185 → 191  | 0.11       | 185 → 191  | 0.10       |
| 185 → 192  | -0.13      | 185 → 192  | -0.15      | 185 → 192  | -0.17      |
| 186 → 192  | -0.11      | 186 → 193  | -0.12      | 186 → 193  | 0.11       |
| 187 → 191  | -0.26      | 187 → 191  | -0.13      | 187 → 191  | 0.10       |
| 187 → 192  | 0.17       | 187 → 192  | -0.16      | 187 → 192  | -0.17      |
| 187 → 193  | -0.10      | 187 → 193  | -0.13      | 187 → 193  | 0.12       |
| 187 → 194  | 0.13       | 190 → 191  | 0.15       | 190 → 191  | 0.14       |
| 190 → 191  | -0.23      | 190 → 192  | 0.40       | 190 → 192  | 0.43       |
| 190 → 192  | 0.33       | 190 → 193  | 0.32       | 190 → 193  | -0.28      |
| 190 → 193  | -0.25      | 186 → 192  | -0.19      | 186 → 192  | 0.19       |
| 186 → 193  | -0.22      | 186 → 192  | -0.20      | 186 → 192  | 0.19       |
| 189 → 191  | -0.12      | 186 → 193  | 0.20       | 186 → 193  | 0.22       |
| 189 → 192  | 0.31       | 189 → 192  | -0.38      | 189 → 192  | 0.34       |
| 189 → 193  | 0.39       | 189 → 193  | 0.39       | 189 → 193  | 0.42       |
| 190 → 192  | -0.15      | 190 → 192  | 0.10       | 190 → 192  | -0.10      |
| 190 → 193  | -0.17      | 190 → 193  | -0.13      | 190 → 193  | -0.13      |

[a] In parentheses transition energies in eV.

[b] HOMO is MO #190.
**Table S7.** Structural exploration of alternative isomers / conformers of the tetramethoxy-substituted compound (monocation, triplet state). In parentheses relative energies (kcal mol\(^{-1}\)) referred to the most stable form (in bold) identified at the specified level.

| # | Isomer / Conformer | Symmetry | \(E_{\text{PCM}} / \text{Ha}^b\) | \(H_{\text{PCM,RRHO}} / \text{Ha}\) | \(G_{\text{PCM,RRHO}} / \text{Ha}\) |
|---|-------------------|----------|-------------------------------|-------------------------------|-------------------------------|
| apical_apical/.../TRIPLET/conf1_5 | apical, apical, conf1_5 | \(C_2\) | 2323.94481 2 (3.5) | 2323.14032 4 (3.2) | 2323.26938 1 (3.2) |
| apical_apical/.../TRIPLET/conf2_5 | apical, apical, conf2_5 | \(C_2\) | 2323.94291 3 (4.7) | 2323.13875 9 (4.2) | 2323.26870 6 (3.6) |
| apical_equatorial/.../TRIPLET/conf1_5 | apical, equatorial, conf1_5 | \(C_2\) | 2323.95032 7 (0.0) | 2323.14541 6 (0.0) | 2323.27373 3 (0.5) |
| apical_equatorial/.../TRIPLET/conf1_6 | apical, equatorial, conf1_6 | \(C_2\) | 2323.95034 0 (0.0) | 2323.14548 4 (0.0) | 2323.27447 3 (0.0) |
| apical_equatorial/.../TRIPLET/conf2_5 | equatorial, equatorial, conf2_5 | \(C_2\) | 2323.94656 8 (2.4) | 2323.14250 6 (1.9) | 2323.27167 5 (1.8) |
| apical_equatorial/.../TRIPLET/conf2_6 | equatorial, equatorial, conf2_6 | \(C_2\) | 2323.94687 0 (2.2) | 2323.14303 6 (1.5) | 2323.27243 8 (1.3) |

[a] For chiral structures, only one enantiomer is listed.

[b] Electronic energy.

**Table S8.** Energies of alternative isomers / conformers of the tetramethoxy-substituted compound (monocation) computed in the first triplet state at the equilibrium geometry of the ground-state singlet. In parentheses relative energies (kcal mol\(^{-1}\)) referred to the most stable form (in bold) identified at the specified level.

| # | Isomer / Conformer | Symmetry | \(E_{\text{PCM}} / \text{Ha}^b\) |
|---|-------------------|----------|-------------------------------|
| apical_apical/.../TRIPLET_AT_SINGLET_GEOM_NONEQ_SOLV/conf1_5 | apical, apical, conf1_5 | \(C_1\) | 2323.92906 2 (0.6) |
| apical_apical/.../TRIPLET_AT_SINGLET_GEOM_NONEQ_SOLV/conf2_5 | apical, conf2_5 | \(C_1\) | - |

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Table S9. Energies of alternative isomers / conformers of the tetramethoxy-substituted compound (monocation) computed for the ground-state singlet at the equilibrium geometry of the first triplet. In parentheses relative energies (kcal mol\(^{-1}\)) referred to the most stable form (in bold) identified at the specified level.

| # | Isomer / Conformer | Symmetry | \(E_{PCM} / \text{Ha}\) |
|---|-------------------|----------|-----------------------------|
| apical_equatorial/.../TRIPLET_AT_SINGLET_GEOM_NONEQ_SOLV/conf1_5 | apical, apical, conf1_5 | \(C_2\) | 2323.92769 9 (1.5) |
| apical_equatorial/.../TRIPLET_AT_SINGLET_GEOM_NONEQ_SOLV/conf1_6 | apical, equatorial, conf1_5 | \(C_2\) | - 2323.92945 6 (0.4) |
| apical_equatorial/.../TRIPLET_AT_SINGLET_GEOM_NONEQ_SOLV/conf2_5 | apical, equatorial, conf1_6 | \(C_2\) | - 2323.93006 8 (0.0) |
| apical_equatorial/.../TRIPLET_AT_SINGLET_GEOM_NONEQ_SOLV/conf2_6 | apical, equatorial, conf2_5 | \(C_2\) | - 2323.92857 3 (0.9) |
| apical_equatorial/.../TRIPLET_AT_SINGLET_GEOM_NONEQ_SOLV/conf2_6 | equatorial, equatorial, conf2_6 | \(C_2\) | - 2323.92911 8 (0.6) |

[a] For chiral structures, only one enantiomer is listed.

[b] Electronic energy.
| Isomer / Conformer                      | Singlet / singlet geometry | Singlet / triplet geometry | Triplet / triplet geometry | Triplet / singlet geometry |
|----------------------------------------|----------------------------|----------------------------|---------------------------|---------------------------|
| apical, apical, conf1_5               | 0.0                        | 10.7                       | 48.5                      | 58.4                      |
| apical, apical, conf2_5               | 1.7                        | 13.1                       | 49.7                      | 59.3                      |
| apical, equatorial, conf1_5            | 1.7                        | 17.8                       | 45.1                      | 58.2                      |
| apical, equatorial, conf1_6            | 1.6                        | 18.0                       | 45.1                      | 57.8                      |
| equatorial, equatorial, conf2_5        | 2.3                        | 16.9                       | 47.4                      | 58.7                      |
| equatorial, equatorial, conf2_6        | 2.1                        | 16.3                       | 47.2                      | 58.4                      |

[a] For chiral structures, only one enantiomer is listed.

[b] Electronic energy.

**Table S10.** Summary of singlet and triplet energies of alternative isomers / conformers of the tetramethoxy-substituted compound (monocation). All energies (kcal mol⁻¹) are referred to the most stable singlet.
Figure S18. UV-Vis spectra computed at the TD-M062X level for several isomers / conformers of the tetramethoxy-substituted compound (monocation, singlet).
Figure S19. Selected molecular orbitals [TD-M062X / 6-31+G(d,p) /PCM] in chloroform. Orbital energies (in hartree) are reported.

| apical, apical, conf1_5 | apical, apical, conf2_5 | apical, equatorial, conf1_5 |
|------------------------|-------------------------|-----------------------------|
| ![Molecular Orbital](image1) | ![Molecular Orbital](image2) | ![Molecular Orbital](image3) |
| 188 (-0.29865)         | 188 (-0.29910)          | 188 (-0.29550)              |
| ![Molecular Orbital](image4) | ![Molecular Orbital](image5) | ![Molecular Orbital](image6) |
| 189 (-0.29598)         | 189 (-0.29601)          | 189 (-0.28767)              |
|       |       |       |
|-------|-------|-------|
| 189 (-0.28763) | 189 (-0.28780) | 189 (-0.28785) |
| 190 (-0.28251) | 190 (-0.28426) | 190 (-0.28419) |
| 191 (-0.08913) | 191 (-0.09083) | 191 (-0.09091) |

[a] Iso-density 0.04 a.u.
Figure S20. Summary of singlet and triplet energies of alternative isomers / conformers of the tetramethoxy-substituted compound (monocation). All energies (kcal mol$^{-1}$) are referred to the most stable singlet.

Summary of singlet and triplet energies

#1-#2: conformers of the apical, apical isomer; #3-#6: conformers of the apical, equatorial isomer

![Graph showing singlet and triplet energies](image-url)
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