Interplay between \( \pi \)-conjugation and Exchange Magnetism in One-Dimensional Porphyrinoid Polymers

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1. General methods and materials

1.1. Synthetic procedures and materials

Synthetic procedures were carried out under an inert argon atmosphere and in dry solvents. All regents and solvents were used as received. Boron trifluoride diethyl etherate solution (purified by redistillation, ≥46.5% BF$_3$ basis), culminaldehyde and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were purchased at SIGMA-Aldrich. 5-mesityldipyromethane was synthesized as described in the literature according to reported methods. All solvents used for reactions and purifications were purchased at Charlau (ISO reagent grade). CDCl$_3$ for NMR experiments was purchased at SIGMA-Aldrich and CHCl$_3$ (spectroscopic grade) for UV-Vis experiments at Charlau. Chromatographic purifications were performed using silica gel 60, 0.040–0.06 mm (230-400 mesh ASTM; Sharlau). Analytical thin-layer chromatography (TLC) was performed using aluminium coated Merck Kieselgel 60 F254.

1.2. Instruments

- **NMR.** $^1$H (400 MHz) and $^1$H-decoupled $^{13}$C (100 MHz) NMR spectra were recorded on a Bruker TopSpin AV-400 spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm) relative signal(s) of the partially deuterated solvents as internal standards. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, and the coupling constants ($J_{HH}$) are given in Hz.

- **UV/Vis** absorption spectra were recorded on an Agilent Cary 50 UV-Vis spectrophotometer at room temperature, using a standard 10 mm UV cuvette (QS). Fluorescence spectra were recorded on an HORRIBA Fluorolog®-3 spectrofluorometer using a 10 mm fluorescence UV cuvette (QS).

- **MS** experiments were performed by the Servicio Interdepartamental de Investigacion (SldI) at the Autonoma University of Madrid. Mass spectra matrix assisted laser desorption ionization coupled to a time of flight analyser (MALDI-TOF MS) experiments were recorded on a Bruker Ultraflex III.

2. Synthesis and characterization of porphyrin 1

![Scheme S1. Synthesis of porphyrin 1; reagents and conditions: i) BF$_3$•OEt$_2$, CHCl$_3$, RT, Ar, 2h, followed by DDQ, RT, 1 h (20%) (DDQ = 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone).](image-url)
Porphyrin 1. A solution of culminaldehyde (0.22 mL, 1.48 mmol) and 5-mesityldipyrromethane\(^1\text{--}^4\) (400 mg, 1.51 mmol) in CHCl\(_3\) containing 0.75% of EtOH (150 ml) was degassed by bubbling argon for 15 min. Afterwards, a 0.793 M solution of BF\(_3\)•Et\(_2\)O in CHCl\(_3\) (0.62 mL, 0.49 mmol) was added and the resulting mixture stirred for 2h at RT under argon. DDQ (510 mg, 2.24 mmol) was then added and the mixture stirred for an additional hour. Finally, few drops of Et\(_3\)N were added to neutralize the acidic media, and then the mixture filtered through a plug of SiO\(_2\) (CHCl\(_3\)) and the solvents evaporated. The resulting solid was purified by column chromatography on SiO\(_2\) (CH\(_2\)Cl\(_2\)/hexanes, 1:1). Purification was achieved by two successive trituration steps, first in hexane then in MeOH, to afford 1 as a dark purple solid (116 mg, 0.148 mmol; Yield 20%). \(^1\)H NMR (400 MHz, CDCl\(_3\), 25°C) \(\delta\)H = 8.88 (d, \(^3\)J(\(\beta_1,\beta_2\)) = 4.7 Hz, 4H; H-\(\beta_1\)), 8.72 (d, \(^3\)J(\(\beta_2,\beta_1\)) = 4.7 Hz, 4H; H-\(\beta_2\)), 8.18 (d, \(^3\)J(\(\alpha,\beta\)) = 8 Hz, 4H; H-\(\alpha\)), 7.62 (d, \(^3\)J(\(m,\alpha\)) = 8 Hz, 4H; H-\(m\)), 7.32 (s, 6H; H-R), 3.28 (sept., \(^3\)J(c,d) = 6.9 Hz, 2H; ArCH(CH\(_3\))\(_2\), H-c), 2.66 (s, 6H; H-b; ArCH\(_3\)), 1.89 (s, 12H; ArCH\(_3\), H-a), 1.57 (d, \(^3\)J(d,c) = 6.9 Hz, 12H; (CH\(_3\))\(_2\)CH, H-d), -2.55 ppm (s, 2H; NH). \(^{13}\)C NMR (75 MHz, CDCl\(_3\), 25°C) \(\delta\)C = 148.1, 139.4, 139.3, 138.6, 137.6, 134.6, 131.4 (br; \(\alpha\)-Cpyrrolic), 129.9 (br; \(\alpha\)-Cpyrrolic), 127.7, 124.8, 119.5, 118.1, 34.1 (ArCH), 24.3 (CH\(_3\)), 21.6 (ArCH\(_3\)), 21.5 ppm (ArCH\(_3\)). UV/Vis (CHCl\(_3\); 25°C): \(\lambda_{max} (\varepsilon)= 419 (443,600), 516 (17,700), 551 (7,470), 591 (5,240), 647 nm (3,580 dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)). MS (MALDI-TOF; DCTB): m/z (%) found: 782.5 (100) [M]\(^+\). HRMS (MALDI-TOF; DCTB + PPGNa 790): m/z calcld for C\(_{50}\)H\(_{54}\)N\(_4\): 782.4343; found 782.4348 [M]\(^+\).

**Figure SI.** UV/Visible absorption (left) and fluorescence (right) spectra of porphyrin 1 in CHCl\(_3\) solution.
**Figure SII.** MALDI-TOF MS spectrum of porphyrin 1 (matrix: DCTB).

**Figure SIII.** HR MALDI-TOF MS spectrum of porphyrin 1 (matrix: DCTB + PPGNa 790).
Figure SIV. $^1$H NMR (CDCl$_3$, 400 MHz) of porphyrin I and proposed assignment (* denotes the residual CHCl$_3$ peak of the CDCl$_3$ solvent).

Figure SV. $^{13}$C NMR (CDCl$_3$, 100 MHz) of porphyrin I (* denotes the signal of the CDCl$_3$ solvent).
3. Experimental and computational methods

Experimental methods
Experiments were performed in a custom-designed ultra-high vacuum system (base pressure below $1 \times 10^{-10}$ mbar) hosting a commercial low-temperature microscope with STM/AFM capabilities from ScientaOmicron and located at IMDEA Nanoscience (Madrid, Spain). The Au(111) single crystal surface was prepared by repeated cycles of Ar$^+$ sputtering ($E = 1$ keV) at a pressure of $2.0 \times 10^{-6}$ mbar and subsequent annealing to 740 K for 10 minutes. Molecular precursor 1 was thermally deposited (Kentax TCE-BSC) onto the clean Au(111) surface held at room temperature with a typical deposition rate of 0.5 Å/min (sublimation temperature of 275.5 °C), controlled by a quartz micro balance (LewVac). After deposition of 1, the sample was post-annealed to 200 °C for 25 min to induce the oxidative ring closure and cyclodehydrogenation reactions. All STM images shown were taken in constant current mode, unless otherwise noted, with electrochemically etched tungsten tips, either pristine or functionalized with CO if necessary, at a sample temperature of 4.3 K (LakeShore). Scanning parameters are specified in each figure caption. Non-contact AFM measurements were performed with a tungsten tip attached to a Qplus tuning fork sensor (Omicron). The tip was a posteriori functionalized by a controlled adsorption of a single CO molecule at the tip apex from a previously CO-dosed surface. The functionalized tip enables the imaging of the intramolecular structure of organic molecules. The sensor was driven at its resonance frequency (~26 kHz for Qplus) with a constant amplitude of ~60 pm. The shift in the resonance frequency of the sensor (with the attached CO-functionalized tip) was recorded in a constant-height mode (ScientaOmicron Matrix electronics and MFLi PLL by Zurich Instruments for ScientaOmicron). The STM and nc-AFM images were analyzed using Wavemetrics Igor Pro and WSxM.
4. Additional experimental and computational results

**Figure S1. Room temperature sublimation of 1 on the Au(111) substrate.** The high-resolution STM image shows the self-assembly arrangement of 1 with its superimposed molecular model. We attributed the self-assembled structure to $\pi \cdots \pi$ interactions between nonplanar segments (benzene rings) of adjacent molecules. Scanning parameters: $V_b = 0.90$ V, $I_t = 70$ pA. Scale bar = 2 nm.
Figure S2. Thermal-induced hydrogen dissociation from the porphyrinoid units. a) Overview STM image of the sample after deposition of a submonolayer coverage of the molecular precursor and subsequent annealing at 280 °C on Au(111). 1D chains coexisting with some disordered patches attributed to unselective C-H bond dissociation are shown. Scanning parameters: \( V_b = 0.5 \text{ V}, I = 10 \text{ pA} \). Scale bar = 10 nm. b) High-resolution STM image of a polymer chain that corresponds to the green rectangle marked in (a). Scanning parameters: \( V_b = -0.95 \text{ V}, I = 30 \text{ pA} \). Scale bar = 1 nm. c) UHR-STM image acquired with a CO-functionalized tip of the segment shown in (b). Herein, only a partial hydrogen dissociation can be observed. Scanning parameters: \( V_b = 5 \text{ mV}, I = 30 \text{ pA}, z_{offset} = -20 \text{ pm} \). Scale bar = 1 nm.
Figure S3. Top and side views of the DFT equilibrium geometry of a segment of polymer 3 on the gold surface. Atoms highlighted in green, white and light blue correspond to carbon, hydrogen and nitrogen atoms respectively. Carbon atoms in the porphyrinoid unit present an adsorption height of 3.4 Å with respect to the underlying surface, compatible with physisorption. The blue and black colored dots serve as a guide to the eye for comparing the features of the top and side view images.
Figure S4. Characterization of the electronic structure of polymer 2 and 3 on Au(111). a,c) Experimental STS acquired at the positions depicted by the colored cross marks in the high-resolution STM insets respectively. The features shown in the $\frac{dI}{dV}$ spectra are assigned to the VBM and the CBM, deducing STS-band gaps of 1.48 eV for polymer 2 and 1.75 eV for polymer 3. Scanning parameters of the insets: $V_b = 1.0 \, V$, $I_t = 100 \, pA$. Scale bars: 1 nm. b,d) Constant-current $\frac{dI}{dV}$ maps acquired with a CO-functionalized tip at the energetic positions corresponding to the conduction band (CB) and valence band (VB) of polymers 2 and 3 respectively. Open feedback parameters, b) VB: $V_b = 0.63 \, V$, $I_t = 250 \, pA$, $V_{rms} = 20 \, mV$, CB: $V_b = 0.85 \, V$, $I_t = 250 \, pA$, $V_{rms} = 20 \, mV$; d) VB: $V_b = 0.85 \, V$, $I_t = 250 \, pA$, $V_{rms} = 20 \, mV$, CB: $V_b = 0.9 \, V$, $I_t = 250 \, pA$, $V_{rms} = 20 \, mV$). In the right panels of b) and d), DFT-calculated LDOS maps of the VB and CB of polymers 2 and 3, are evaluated at a height of 4 Å above the molecular plane.
Single porphyrinoid unit models: DFT and many-body calculations

To understand the electronic structure and underlying $\pi$-conjugation resonant form we carried out total energy DFT calculations of the full and reduced models of porphyrinoid single unit, see Figure S5. The DFT calculations show that the ground state for both models is triplet ($S = 1$) biradical state, with two unpaired electrons located on the opposite side of the porphyrinoid unit. The first excited singlet state ($S = 0$) is 13 meV for the porphyrinoid model above the ground state. Note that both considered porphyrinoid models possess very similar electronic structure, see Figure S6. This justifies the application of the reduced model for computationally more demanding many-body calculations (see later on).

![Figure S5](image1.png)

**Figure S5.** Atomic structure of different porphyrinoid models and corresponding spin density of the ground state $S = 1$ triplet state; a) periodic porphyrinoid chain; b) bare porphyrinoid unit; and c) reduced porphyrinoid.

![Figure S6](image2.png)

**Figure S6.** Comparison of the electronic structure of the a) bare and b) reduced porphyrinoid models of the ground state $S = 1$ triplet state obtained from the DFT calculations at PBE0 level.

We also carried out ACID calculations and bond length analysis to obtain further insight into the $\pi$-conjugation resonant form of the porphyrinoid unit. Figure S7 displays ACID plot of both models as well as the bare porphyrinoid unit for comparison. The comparison of ACID with the bare porphyrin unit shows quite very distinct scenario. This confirms completely different scenario of porphyrinoid units than the bare porphyrin. Namely, quite disjunctive characters of the paramagnetic part of the
current density in central part may also counts for relatively low exchange interaction between two radical states located on the periphery.

Figure S7. ACID analysis of a) bare, b) reduced porphyrinoid models and c) porphyrin unit calculated in the gas phase. Red arrows indicate aromatic diatropic and blue arrows anti-aromatic paratropic ring current. Isovalue = 0.055 a.u.

Figure S8. Comparison of bond length analysis of the a) bare and b) reduced porphyrinoid models and c) porphyrin unit.

To confirm the validity of the DFT calculations, we carried out series many-body calculations of the reduced porphyrin unit with different level of accuracy. We employed only the reduced model, which makes the many-body calculations computationally trackable in reasonable time framework. In all cases, we have found the triplet $S = 1$ ground state and first excited state corresponding to single $S = 0$ state. Table S1 summarizes the energy difference between the ground triple $S = 1$ and the first excited singlet $S = 0$ states for DFT and many-body calculations. The comparison shows that the single-determinant DFT method describes reasonably well the electronic structure of the porphyrinoid chain.
|                | reduced model | full model |
|----------------|---------------|------------|
| $\Delta E_{S1-S0}$ [meV] | 23 72 44 26 38 14 21 |

**Table S1.** Energy difference between the ground $S = 1$ and first excited $S = 0$ states of two porphyrinoid models using different theoretical methods.

**Figure S9.** Analysis of the spectral features after sequential tip-induced hydrogen removal to form polymer 3. a) $d\bar{I}/dV$ spectrum shown in position $\alpha$ of Figure 3b, fitted using the Frota function including the vibration fit (red line) and the vibration plus spin-flip fits (blue line). Clearly the fit depicted by the blue line reproduces much better the observed spectral features which further support the existence of a ferromagnetic (triplet) ground state of a porphyrinoid unit predicted by DFT calculations. b) $d\bar{I}/dV$ spectrum shown in position $\alpha$ of Figure 3c showing the nice fitting (blue dashed line) to a single Frota function. The fit is now very satisfactory without the spin-flip component. c) Raw $d\bar{I}/dV$ spectra showing the comparison between the spectra acquired at position $\alpha$ in Figure 3b (red line) and Figure 3c (blue line). The disappearance of the additional signal located next to the central Kondo feature and attributed to a spin-flip signal is clearly observed.

| Spectrum                  | 1            | 2            | 3            |
|--------------------------|--------------|--------------|--------------|
| $I_K$ (mV)               | 2.9          | 3.5          | 2.5          |
| Frota amplitude          | $1.36 \times 10^{-10}$ | $1.62 \times 10^{-10}$ | $2.07 \times 10^{-10}$ |
| Frota line-shape         | 3.164        | 3.153        | 3.145        |
| $J$ (mV)                 | 11.9         | 11.9         | -            |
| $I_{TS}$ (mV)            | 5.9          | 9.4          | -            |
| Spin flip amplitude      | 0.027        | 0.058        | -            |

**Table S2.** Parameters obtained from the fits depicted in Figure S9.
Details of Fitting procedure
Spectra have been fitted using Python 3.7, Numpy and SciPy. Spectra where loaded into the Python environment with access2theMatrix. The Frota function as used here already took into account the inverse of the factor 2.542, so that the output was directly related to the HWHM of the feature. To account for the CO vibrations present at around 32 mV, two Fermi-Dirac functions where used, symmetric with respect to the Fermi level. We also allowed for offset and a linear background of the spectra. For the spin-flip triplet–singlet side peaks we used a similar formalism as in reference. We did however substitute the Lorentzian line shapes for a Frota line shape for the central feature, and a Fano line shape for the triplet–singlet side peaks. With this formalism one obtains values for the Kondo resonance width ($\Gamma_K$), the width of the triplet-singlet excitation ($\Gamma_{TS}$), and the coupling strength between the spins ($J$). We observed that $\Gamma_{TS}$ depends on the local molecular environment, and can be different for both sites on a single porphyrin molecule (Table S1), however the $J$ is the same for both sites as would be expected.
**Dimer porphyrinoid models: DFT & CAS+DFT**

**Figure S10.** Schematic figure labels four possible radical states in the porphyrinoid dimer model adopted to estimate effective magnetic exchange interactions between individual radical states labeled as $\alpha$-$\delta$.

In the next, we carried out total energy DFT and CAS+DFT simulations of the biradical dimer porphyrinoid. The radical configuration corresponds to the doubly dehydrogenation of the porphyrinoid chain. From the DFT simulations we can deduce that the magnetic interaction between two radicals located on the same porphyrinoid units has an effective ferromagnetic exchange coupling $J_{\text{eff}}^{\text{intra}} = 14$ meV, while the exchange interaction between two radicals located on adjacent porphyrinoid units is either antiferromagnetic $J_{\text{eff}}^{\text{inter}} = -7$ meV (two neighbor sites $\beta,\gamma$ in Figure S10) or negligible for distant radical sites (radical pairs $\alpha,\delta$; $\alpha,\gamma$ or $\beta,\delta$ in Figure S9).

We also carried out many-body CAS+DFT calculations of the biradical dimer model confirming the scenario depicted by the DFT calculations. Namely, CAS+DFT method predicts for the dimer $\alpha,\beta$ model the triplet $S = 1$ ground state (ferromagnetic), while the first excited state is singlet at 22 meV above the triplet ground state. In the case of the dimer $\beta,\gamma$ model, we identify the singlet $S = 0$ ground state (antiferromagnetic) and the first triplet excited state ~ 9 meV above the ground state. In the case of other possible dimer models ($\alpha,\gamma$ and $\alpha,\delta$ configuration, respectively), we found both singlet and triplet states to be degenerated within the expected accuracy (< 1 meV). This indicates that two radicals do not communicate each other in these particular biradical configurations.

| BIRADICAL | $\Delta E_{S1-S0}$ [eV] |
|-----------|-------------------|
| $\alpha\beta$ | 0.014             |
| $\alpha\gamma$ | 0.000             |
| $\alpha\delta$ | 0.000             |
| $\beta\gamma$ | -0.007            |

**Table S3.** Energy difference between the ground $S=1$ and first excited $S=0$ states of the biradical porphyrinoid dimer using DFT PBE0 calculations. For labeling distinct spin configuration of the porphyrinoid dimer see Figure S10.
Computational details

Total energy DFT calculations

Total energy calculations were carried out using density functional theory (DFT) calculations using the FHI-AIMS code with light settings for the atomic basis sets. Infinite chain, monomer and dimers were calculated with hybrid exchange-correlation functional PBE0. In the slab case, the GGA-PBE approximation of the exchange-correlation potential was employed instead of the hybrid functional due to computational feasibility. All the DFT calculations took into account the Tkatchenko-Scheffler treatment of the Van der Waals interactions. The relaxed freestanding porphyrinoïd chain was placed on the Au(111) surface, made of three layers. A 7x10 rectangular supercell was used. All the atoms of the unit cell were thoroughly relaxed, except the last Au layer. The structural optimization was carried up until the total energy and the remaining atomic forces were below 10^-5 eV and 10^-2 eV/Å and respectively. A 10x1x1 k-mesh sampling was used for the integration of the Brillouin zone.

Anisotropy of the Induced Current Density (ACID) was calculated in Gaussian16 package at UB3LYP/def2-SVP level of theory and plotted using the code ACID version 3.0.3. Only π-orbitals were included in the calculation.

Theoretical AFM and dI/dV maps were calculated by the Probe Particle Scanning Probe Microscopy (PP-SPM) code for a CO-like tip, which was represented by a linear combination of PxPy (85%) and s-like (15%) orbitals without tip relaxation. The AFM simulations were performed with an effective charge of -1e and a lateral stiffness of (k) = 0.25 N/m. The Hartree potential used, to determine the electrostatic forces and the Pauli repulsion, were derived from DFT calculations.

Many-body calculations of single porphyrinoid unit

For DMRG studies, we employed the DFT optimized singlet state geometry of the reduced porphyrinoid unit. As a first step, we performed the DMRG-SCF/cc-pVDZ singlet and triplet state orbital optimizations with fixed bond dimensions M=1000 in the full π-complete active space (CAS), in particular the active space comprising 42 electrons in 40 orbitals, CAS(42,40), denoted as CASSCF in Table S1. The final orbitals were split-localized by means of the Pipek-Mezey procedure for the subsequent refining DMRG calculations with the dynamical block state selection and a pre-defined truncation error TRE = 10^-5, which were initialized with the CI-DEAS procedure. These DMRG calculations (denoted as DMRG in Table S1) were used to generate the one- and two-electron reduced density matrices for the adiabatic connection (AC) dynamical electron correlation correction. Due to a high computational cost connected with the full AC integration, we carried out the linearized-AC-integrand approximation named AC0, which was shown on many different examples to offer accuracy similar to or exceeding that of NEVPT2. All DMRG calculations were performed with the MOLMPS program with machine learning extensions, which was for the purposes of DMRG-SCF interfaced to Orca.

CAS+DFT of porphyrinoid dimers

To calculate the ground-state and low-energy excited state and corresponding many-body wavefunctions of selected porphyrinoid dimers, we use as a home-built many-body CAS+DFT method to solve the extended Hubbard Hamiltonian including the π-electrons of the system only:

$$\mathcal{H} = \sum_{\mu,\nu,\sigma} t_{\mu\nu} \hat{c}_{\mu\sigma}^+ \hat{c}_{\nu\sigma} + \text{h.c.} + \sum_{\mu} U \hat{n}_{\mu\uparrow} \hat{n}_{\mu\downarrow}$$

where $\mu,\nu$ means π-orbitals on carbon and nitrogen atomic sites and $\sigma$ is spin index. We constructed one-electron Hamiltonian consisting of π-orbitals of carbon and nitrogen atoms using a closed shell SCF solution obtained from DFT calculation with the software Fireball using the BLYP functional
and a minimal basis set of pseudo-atomic orbitals. Namely, we extracted the hoppings $t_{\mu \nu}$ between different atomic sites $\mu, \nu$ from DFT self-consistent simulations using the optimized structure taken from the total energy DFT calculations. We consider Coulombic repulsion, $U$, to be 4.2 eV for both carbon and nitrogen $\pi$-orbitals.\(^3\) Note that we found that variation of parameter $U$ in a range from 3 eV to 6 eV for nitrogen has a very little impact on the ground and first excited state, varying the energy difference in less than 1%.

Next, we rewrite the extended Hubbard Hamiltonian (originally in terms of the creation/annihilation operators $\hat{c}_{\mu \sigma}^+, \hat{c}_{\mu \sigma}$ of the atomic sites $\mu$) in terms of the creation/annihilation operators $\hat{C}_{j \sigma}^+, \hat{C}_{j \sigma}$ of the molecular orbitals $j$ obtained from the DFT Hamiltonian in the Löwdin basis corresponding to the subspace of $\pi$-orbitals as follows:

$$\hat{c}_{j \sigma} = \sum_{\mu} \phi_{j, \mu} \hat{c}_{\mu \sigma}$$

where $\phi_{j, \mu}$ are the coefficients of the expansion of the $j$-th molecular orbital over the basis of atomic sites $\mu$. By changing basis from atomic orbitals to molecular orbitals we write the extended Hubbard Hamiltonian:

$$\hat{H} = \sum_{j,k,\sigma} T_{jk} \hat{C}_{j \sigma}^+ \hat{C}_{k \sigma} + h.c. + \sum_{j,k,l,m} U_{jklm} \hat{C}_{j \uparrow}^+ \hat{C}_{k \downarrow} \hat{C}_{l \downarrow} \hat{C}_{m \uparrow}$$

In the many-body calculation we keep only up to six $j$-th molecular orbitals (centered around the Fermi level). The choice of the active space consisting of 6 molecular orbitals is justified by an analysis of the occupancies of the natural orbitals.\(^3\) Note, that the occupancy of natural orbitals also provides valuable information about the open-shell character of the system\(^3\) although the starting active space of molecular orbitals was obtained from the close -shell DFT calculations.
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