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Monitoring aromatic ring-currents in Mg-porphyrin by time-resolved circular dichroism†

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Time-resolved circular dichroism signals (TRCD) in the X-ray regime can directly probe the magnitude and the direction of ring currents in molecules. The electronic ring currents in Mg-porphyrin, generated by a coherent superposition of electronic states induced by a circularly polarized UV pulse, are tracked by a time-delayed circularly polarized attosecond X-ray pulse. The signals are calculated using the minimal coupling Hamiltonian, which directly makes use of transition current densities. The TRCD signals obtained from the left and right circularly polarized light pump have opposite signs, revealing the direction of the ring current. Molecular aromaticity and its role in photochemical reactions such as ring opening or closure can be studied using this technique.

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Introduction

Exploring and controlling the dynamics of aromatic ring currents has received great attention for decades. Ring currents have been used to quantify the aromaticity of ring molecules.^{1–3} Their magnitude has been compared with the nucleus-independent chemical shift⁴ or diamagnetic susceptibility exaltation value⁵ and used to determine the aromaticity of molecules. Aromatic ring currents and their induced magnetic fields have been recently used for nanodevices,^{6–10} such as molecular magnets,⁶ quantum devices,⁷ and photo-switches,^{9–11} and to generate ultrafast magnetic field pulses.⁸

An aromatic ring current is generated by a magnetic field perpendicular to the molecular plane due to the delocalized π electrons.¹² A more effective way to create ring currents using circularly polarized light^{6,13,14} was suggested by the Manz group: the chirality of the laser pulse is transferred to the molecular system, inducing a clockwise or counterclockwise ring current. This current is much stronger than what can be induced by an external magnetic field with present technology.⁶ For example, in a Mg-porphyrin molecule, the net ring current induced by a circularly polarized laser π -pulse corresponds to one induced by a magnetic field of 8048 T, which is 100 times

higher than the maximum permanent magnetic field currently available.⁶

So far, monitoring the ultrafast circular coherent dynamics of ring currents in real time has been a challenge. Many experimental and computational approaches have been developed for the indirect measurement of aromatic ring currents: nuclear magnetic shielding,^{15,16} current density³ and bond order,¹⁷ and polarizability analysis.^{18,19}

Several studies have attempted the direct observation of aromatic ring currents. Yuan *et al.*²⁰ and Wollenhaupt *et al.*²¹ measured molecular angular and energy-resolved photoelectron spectra by using time-delayed X-ray pulses. Neufeld *et al.*²² proposed that high-harmonic generation in the presence of a ring current causes the emission of elliptically polarized harmonics. Koksai *et al.*²³ showed the possible manipulation of a ring current and induced magnetic field by changing the frequency and the orbital angular momentum of the light beams. However, both photoelectron circular dichroism and high-harmonic generation require elaborate experimental setups and are hard to interpret. Here, we discuss the use of time-resolved X-ray circular dichroism (TRCD) to directly measure the fast electronic motions associated with ring currents.

Attosecond X-ray pulses provide real-time and real-space resolution of electronic structure, enabling the creation of molecular movies.²⁴ The high-spatial resolution of X-rays can reveal local properties in delocalized aromatic systems.

CD spectra are usually weak signals on top of a large achiral background. Transient CD signals are usually measured on top of a static background. The use of X-ray excitation from valence excited states allows one to generate transitions below the pre-edge region, a frequency regime with no or low static background. The absence of a static achiral background induces a large asymmetry

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ratio (>100%, eqn (10) below) compared to standard CD techniques (a few % or less).

In this paper, we study the use of time-resolved circular dichroism (TRCD) signals to probe ring currents: a UV pump pulse induces a ring current and a delayed X-ray probe measures the induced dichroic signal. The magnitude and the sign of the signal reveal the amplitude and the direction of the ring current. We employ the minimal coupling Hamiltonian for the light-matter interaction, which expresses the signal directly in terms of transition current densities. Simulations are carried out for Mg-porphyrin where the X-ray probe is tuned to the nitrogen K-edge at 409 eV or to the magnesium K-edge at 1327 eV.

Theory and computational details

The time-resolved CD signal

The minimal coupling Hamiltonian for the resonant radiation-matter interaction is

$$H_{\text{int}} = -\int d\mathbf{r} \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}, t) \quad (1)$$

where $\mathbf{A}(\mathbf{r}, t)$ is the electromagnetic vector potential of the incoming field and $\mathbf{j}(\mathbf{r})$ is the current-density operator:

$$\mathbf{j}(\mathbf{r}) = \frac{e\hbar}{2mi} [\psi^\dagger(\mathbf{r}) \nabla \psi(\mathbf{r}) - [\nabla \psi^\dagger(\mathbf{r})] \psi(\mathbf{r})] \quad (2)$$

where $\psi^\dagger(\mathbf{r})$ and $\psi(\mathbf{r})$ are the electron field creation and annihilation operators at position $\mathbf{r}$.

The time-dependent density matrix after two interactions with the pump pulse (Fig. S2, ESI†) is given by

$$\begin{aligned} \rho_{ee'}(T) &= \langle \langle ee' | \rho(T) \rangle \rangle \\ &= \left(\frac{-i}{\hbar} \right)^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_1 d\mathbf{r}_2 \langle \langle ee' | \mathbf{j}_-(\mathbf{r}_2, t_2) \mathbf{j}_-(\mathbf{r}_1, t_1) | \rangle \rangle \\ &\quad \times \rho(T - t_1 - t_2) \rangle \rangle \mathbf{A}_{\text{pu}}^*(\mathbf{r}_2, T - t_2) \mathbf{A}_{\text{pu}}(\mathbf{r}_1, T - t_2 - t_1) \\ &= \left(\frac{-i}{\hbar} \right)^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_1 d\mathbf{r}_2 \left[\langle \langle ee' | \mathcal{G}(t_2) \mathbf{j}_{\text{right}}(\mathbf{r}_2) \mathcal{G}(t_1) \mathbf{j}_{\text{left}}^\dagger(\mathbf{r}_1) | \rangle \rangle \right. \\ &\quad \times \rho(t_0) \rangle \rangle \mathbf{A}_{\text{pu}}^*(\mathbf{r}_2, T - t_2) \mathbf{A}_{\text{pu}}(\mathbf{r}_1, T - t_2 - t_1) \\ &\quad + \langle \langle ee' | \mathcal{G}(t_2) \mathbf{j}_{\text{left}}^\dagger(\mathbf{r}_2) \mathcal{G}(t_1) \mathbf{j}_{\text{right}}(\mathbf{r}_1) | \rho(t_0) \rangle \rangle \\ &\quad \times \mathbf{A}_{\text{pu}}(\mathbf{r}_2, T - t_2) \mathbf{A}_{\text{pu}}^*(\mathbf{r}_1, T - t_2 - t_1) \rangle \rangle \end{aligned} \quad (3)$$

$\mathbf{A}_{\text{pu}}$ is the vector potential of the pump and $\mathcal{G}$ is the field free molecular propagator, and $\mathbf{j}_-$ denotes the current density superoperator.²⁵ Here, the subscripts left and right indicate the superoperators defined by $O_{\text{left}}\rho = O\rho$ and $O_{\text{right}}\rho = \rho O$.

In the impulsive limit, the density matrix at waiting time T becomes:

$$\begin{aligned} \rho_{ee'}(T) &= -\frac{1}{\hbar^2} \int \frac{d\omega_1 d\omega_2}{2\pi} \mathbf{A}_{\text{pu}}(\omega_1) \mathbf{A}_{\text{pu}}(\omega_2) \\ &\quad \times \left[\frac{\mathbf{j}_{e'g}(\mathbf{k}_{\text{pu}}) \cdot \mathbf{e}_{\text{pu}}^* \cdot \mathbf{j}_{eg}^*(-\mathbf{k}_{\text{pu}}) \cdot \mathbf{e}_{\text{pu}} e^{i(\omega_2 - \omega_1)T}}{(\omega_1 - \omega_2 - \omega_{ee'} + i\Gamma_{ee'}) (\omega_1 - \omega_{eg} + i\Gamma_{eg})} \right. \\ &\quad \left. + \frac{\mathbf{j}_{eg}^\dagger(-\mathbf{k}_{\text{pu}}) \cdot \mathbf{e}_{\text{pu}} \cdot \mathbf{j}_{e'g}(\mathbf{k}_{\text{pu}}) \cdot \mathbf{e}_{\text{pu}}^* e^{-i(\omega_2 - \omega_1)T}}{(-\omega_1 + \omega_2 - \omega_{ee'} + i\Gamma_{ee'}) (-\omega_1 - \omega_{ge'} + i\Gamma_{ge'})} \right] \quad (4) \end{aligned}$$

where $\mathbf{e}$ are the electric field polarization vectors, which can be left or right polarization. ω_1 and ω_2 run over the bandwidth of the UV pump, which is set on resonance with a specific valence excited state. The dephasing rate, $\Gamma = 200 \text{ cm}^{-1}$, is taken to be the same for all transitions.²⁶

The heterodyne detected signal^{27,28} is given by:

$$S(\Gamma) = -\frac{2}{\hbar} \text{Im} \int d\mathbf{r} d\mathbf{t} \langle \mathbf{j}(\mathbf{r}, t) \cdot \mathbf{A}_{\text{pr}}^*(\mathbf{r}, t) \rangle \quad (5)$$

where Γ indicates the set of pulse parameters, *i.e.* central frequencies, durations, *etc.*, and $\mathbf{A}_{\text{pr}}$ is the vector potential of the probe pulse. Expanding to first order in the probe and taking the difference between the left and the right polarization of the probe we obtain:

$$\begin{aligned} S_{\text{CD}}(\mathbf{k}_s, \omega_s, T) &= \frac{2}{\hbar^2} \text{Re} \int d\mathbf{r} d\mathbf{t} d\mathbf{r}_1 d\mathbf{t}_1 \mathbf{A}_{\text{pr}}^*(\mathbf{r}, t) \mathbf{A}_{\text{pr}}(\mathbf{r}_1, t - t_1) \\ &\quad \times (\mathbf{e}_{\text{L}}^* \mathbf{e}_{\text{L}} - \mathbf{e}_{\text{R}}^* \mathbf{e}_{\text{R}}) \langle \langle \mathbf{j}(\mathbf{r}) | \mathcal{G}(t_1) \mathbf{j}_-(\mathbf{r}_1) | \rho(t - t_1) \rangle \rangle \quad (6) \end{aligned}$$

where the subscript L (R) refers to left (right) circular polarization. Assuming incoming pulses incident along z , using $\mathbf{e}_{\text{L}}^* \mathbf{e}_{\text{L}} - \mathbf{e}_{\text{R}}^* \mathbf{e}_{\text{R}} = (-i)\varepsilon_{abz}$ where ε_{abz} is the Levi-Civita symbol, and summing over electronic eigenstates gives:

$$\begin{aligned} S_{\text{CD}}(\mathbf{k}_s, \omega_s, T) &= \frac{2}{\hbar^2} \text{Im} \sum_{ee'} \int d\mathbf{t} d\mathbf{t}_1 \mathbf{A}_{\text{pr}}^*(\mathbf{r}, t) \mathbf{A}_{\text{pr}}(\mathbf{r}_1, t - t_1) \rho_{ee'}(t - t_1) \\ &\quad \times \left[\mathbf{j}_{e'c}(\mathbf{k}_s) \times \mathbf{j}_{ce}^\dagger(-\mathbf{k}_s) e^{i(\omega_s - \omega_{ce'})t_1 - \Gamma_{ce'}t_1} \right. \\ &\quad \left. - \mathbf{j}_{e'c}^\dagger(-\mathbf{k}_s) \times \mathbf{j}_{ce}(\mathbf{k}_s) e^{i(\omega_s - \omega_{ce})t_1 - \Gamma_{ce}t_1} \right] \quad (7) \end{aligned}$$

where ω_s denotes the detection frequency of the probe pulse. e and e' denote valence excited states $\{e_1, e_2, \dots, e_g\}$ and c denotes core excited states $\{c_1, c_2, \dots, c_{10}\}$ and $\rho_{ee'}$ is given by eqn (4). $\mathbf{j}_{ce}$ and ω_{ce} refer to the core/valence transition current density matrix elements and the transition frequencies, respectively. $\times$ between transition current density terms,

i.e. $j_{e'c}(\mathbf{k}_s) \times j_{ce'}^\dagger(-\mathbf{k}_s)$, indicates a cross product. The final TRCD expression becomes:

$$S_{CD}(\omega_s, T) = \frac{2}{\hbar^2} \frac{1}{(2\pi)^2} \text{Re} \sum_{e'e'} A_{pr}^*(\omega_s) A_{pr}(\omega_s) \rho_{e'e'}(T) \times \left[\frac{j_{e'c}(\mathbf{k}_s) \times j_{ce'}^\dagger(-\mathbf{k}_s)}{\omega_s - \omega_{e'e'} + i\Gamma_{e'e'}} - \frac{j_{ce}(\mathbf{k}_s) \times j_{ec'}^\dagger(-\mathbf{k}_s)}{-\omega_s - \omega_{ec} + i\Gamma_{ec}} \right] \quad (8)$$

Details on the TRCD signal derivation can be found in the ESI.†

The pump-probe setup

We assume a left circularly polarized UV pump propagating along the z direction. The Mg-porphyrin molecule (Fig. 1a) is in the xy plane. If the molecule were placed out of this plane, projections of the incoming field polarizations onto the molecular plane would have to be considered without providing extra insights on the ring current dynamics. After a waiting time T , left and right circularly polarized X-ray probes are used to induce the CD signal. Two Gaussian pumps were considered (Fig. 1c): a narrow 0.1 eV bandwidth Fourier-transform-limited pump (central frequency at 3.125 eV, 18.2 fs duration) selectively excites the e_1 or e_2 states and a broad 1.0 eV bandwidth pump (central frequency at 5.400 eV, 1.82 fs duration) excites all valence excited states except e_1 and e_2 . The X-ray probe at the

N K-edge has a central frequency of 409 eV and 10 eV bandwidth (182 as pulse duration). At the Mg K-edge, we used a 1327 eV central frequency and 10 eV bandwidth (182 as duration).

Electronic structure calculations

Numerical simulations were carried out for Mg-porphyrin (Fig. 1a). Porphyrins are biologically important molecules involved in the primary events of photosynthesis, and biological sensing. Mg-porphyrin has been used as a model system for the generation of ring currents under an external magnetic field or circularly polarized light. Its aromatic ring currents and induced magnetic field with spectroscopic properties have been reported in numerous experimental²⁹ and theoretical studies.^{30,31}

The ground state geometry was optimized at the Hartree-Fock level with the 6-31G(d) basis set using the MOLPRO program.³² A CASSCF (13o/18e) calculation was used to compute transition current density matrix elements between valence states and to validate our results by comparison with previous studies. Because MOLPRO does not provide the one-body reduced transition density matrix needed to compute the current and charge density matrix elements between different wavefunction symmetries, the transition density matrix elements were calculated for C_1 wavefunction symmetry. Transition current density matrix elements were then computed from the transition density matrix based on the optimized geometry. Nine valence excited states and

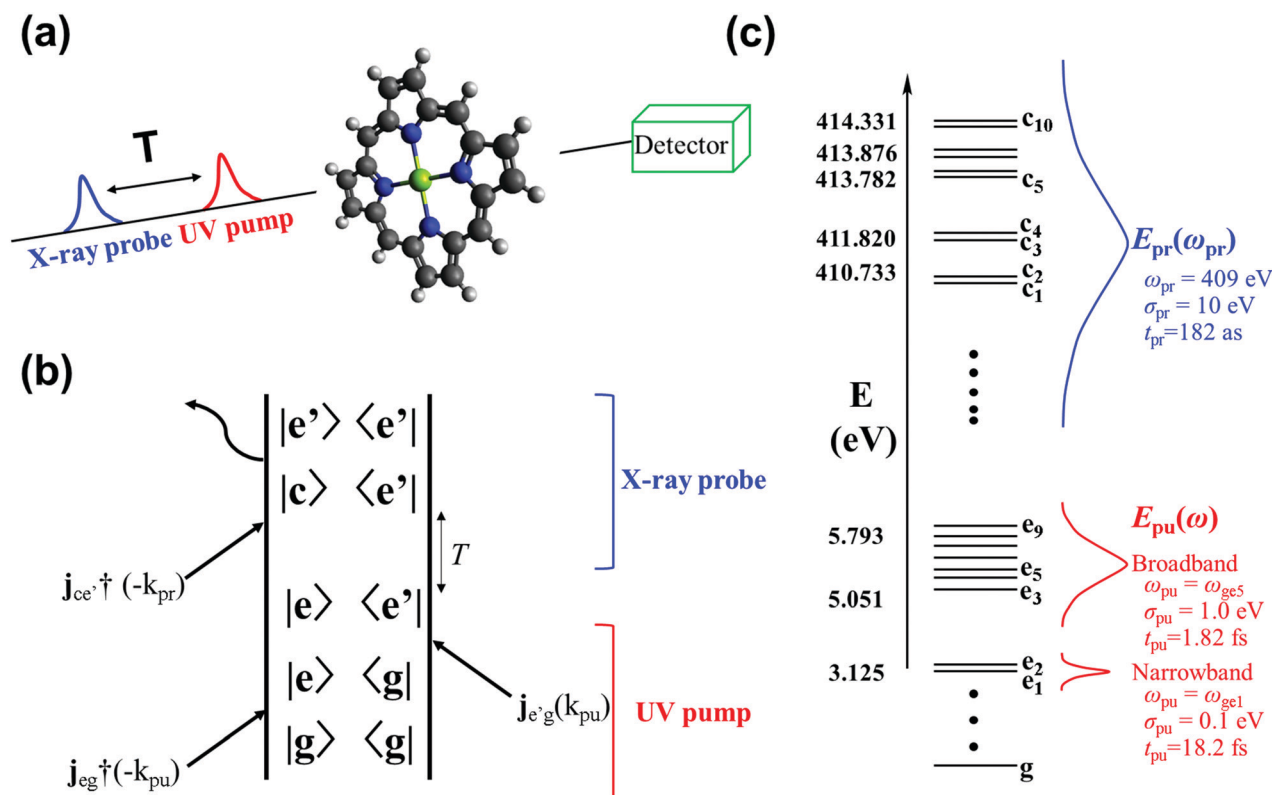


Fig. 1 (a) The Mg-porphyrin used in this study. Gray, white, blue, and yellow spheres represent carbon, hydrogen, nitrogen, and Mg atoms, respectively. (b) Ladder diagram, and (c) the pump/probe setup used to calculate the TRCD signal and electronic energy levels contributing to the signal. Valence manifolds are denoted $\{e_1, e_2, \dots, e_9\}$, while core excited states are denoted $\{c_1, c_2, \dots, c_{10}\}$. $\omega_{pu/pr}$, $\sigma_{pu/pr}$, and $t_{pu/pr}$ denote the central frequency, bandwidth, and the time duration of the pump/probe pulse, respectively.

ten core excited states at the nitrogen K-edge were included for the spectroscopic calculations to match the bandwidth of the incoming pulses. The four degenerate N 1s molecular orbitals were rotated into the active space to calculate the transition density matrix element between valence and core excited states. Similarly, the single Mg 1s molecular orbital was rotated into the active space to generate ten core excited states at the Mg K-edge. Our quantum simulation results were consistent with the previous work of Rubio³³ in terms of transition energies, transition dipole moments, and the orbital configuration of each excited state. Note that e_1 , e_2 , e_3 , e_5 , and e_7 are optically allowed E_u states, where e_1 and e_2 originate from a doubly degenerate state, while e_3 , e_5 , and e_7 do not have degenerate pairs within our computation. e_4 , e_6 , e_8 , and e_9 are optically dark states (see Tables S1 and S2 in the ESI† for more details).

Results and discussion

The transition current densities which generate the ring current are shown in Fig. 2. We display three coherences: $j_{e_1e_2}$, $j_{e_4e_9}$, and $j_{e_6e_8}$. These ring currents have the same magnitude and a constant direction of the transition current density vectors along the porphyrin ring. e_1 and e_2 are degenerate and belong to the same E_u symmetry (B_{3u} and B_{2u} for D_{2h}), and hence their coherence generates a directional ring current, which maintains a clockwise ring current for a long time.³⁴ In contrast, e_4 and e_8 have A_{2g}/B_{2g} (B_{1g} in D_{2h}) symmetry, while e_6 and e_9 have A_{1g}/B_{1g} (A_g in D_{2h}) symmetry. e_4 and e_9 have a degenerate transition from the same $3B_{3g}$ orbital to degenerate $4B_{2g}$ and $4B_{3g}$ orbitals. Similarly, e_6 and e_8 have a degenerate transition from the same $3B_{2g}$ orbital to degenerate $4B_{2g}$ and $4B_{3g}$ orbitals. Although they have different wavefunction symmetries, it is possible to generate a ring current by coherent excitation of two quasi-degenerate excited states with different symmetries.³⁴ e_6 and e_8 have 0.17 eV splitting and e_4 and e_9 have 0.52 eV splitting, and thus $j_{e_4e_9}$ and $j_{e_6e_8}$ generate a coherent ring current which shows beating signals by reversing its rotational direction periodically,³⁴ as will be discussed below. Because e_4 , e_6 , e_8 , and e_9 are all optically

dark states, we mainly probe the ring current generated by e_1e_2 in the following discussions.

There exist quasi-ring currents $j_{e_1e_5}$, $j_{e_2e_3}$, $j_{e_4e_6}$, and $j_{e_5e_7}$; they have a constant clockwise ($j_{e_1e_5}$ and $j_{e_2e_3}$) or counter-clockwise ($j_{e_4e_6}$ and $j_{e_5e_7}$) ring current but the magnitude of the vectors differs and some local vectors exist which do not follow the whole ring current direction. This is apparent for $j_{e_2e_3}$ and $j_{e_4e_6}$ where the local ring currents at the top and bottom could be dominating over the vorticity of the whole ring current.

The current density diagonal matrix elements vanish in all cases. Eqn (8) shows that the cross product of $j_{ec}(k_s) \times j_{cc}^i(-k_s)$ is 0. Hence, the TRCD signal originates from electronic coherence, not from populations. The TRCD signal thus directly probes the electronic coherences between electronic states.

The TRCD signals for the left circularly polarized narrow-band UV pump (0.1 eV) are shown in Fig. 3a–c. Due to the narrow bandwidth only the coherence e_1e_2 contributes to the signal because the Raman pathways of the pump do not contribute to the signal: the only final state available for Raman interaction with the pump is the ground state, where $j_{gc}(k_s) \times j_{cc}^i(-k_s) = 0$ (eqn (8)). This is confirmed by the oscillatory variation of the TRCD signal (Fig. 3b). The TRCD signal decays slowly after the incident pump is switched off³⁵ because e_1 and e_2 are almost degenerate (0.03 eV splitting). The coherence between states with large energy splitting will produce a quickly oscillating signal. The TRCD signal variation with the probe frequency ω_s (Fig. 3c) shows overlapping double peaks near 407.6 eV, reflecting small energy splitting between the e_1 and e_2 states and the degeneracy of the c_1 and c_2 core states. The contributions from the other core excited states, c_3 to c_{10} , are negligibly small and they are invisible in the signal.

Fig. 3d–f present the TRCD signal for the right circularly polarized narrowband UV pump. This signal exhibits a reversed sign but with the same magnitude. The sign of the TRCD signal is thus a direct measure of the direction of the ring current. It also indicates that degeneracy is the key to maintaining long-lasting ring current, because a large energy gap will lead to a quickly oscillating signal. The expectation value of transition current density $j_{e_1e_2}$ in real space vs. the pump–probe waiting time is determined by $\rho(T)$,

$$\langle j_{e_1e_2}(r, T) \rangle = \sum_{a,b=g,e_1,e_2} j_{ab}(r) \rho_{ba}(T) \quad (9)$$

Fig. 4 shows that $\rho(T)$ changes its sign around 100 fs and 200 fs. The magnitude of the ring current decreases in time and eventually changes its direction from clockwise to counter-clockwise at 120 fs. Because the magnitude of the cross product $j_{ec}(k_s) \times j_{cc}^i(-k_s)$ is time-independent, the signal will vary with the pump–probe waiting time, T . The absolute value of the TRCD signal thus directly reflects the magnitude of the ring current in real space.

To investigate the element-sensitivity of TRCD in the presence of ring currents, we compare TRCD signals with the probe tuned at the N or Mg K-edges. To compare signals in such different frequency regimes, it is customary to define the CD

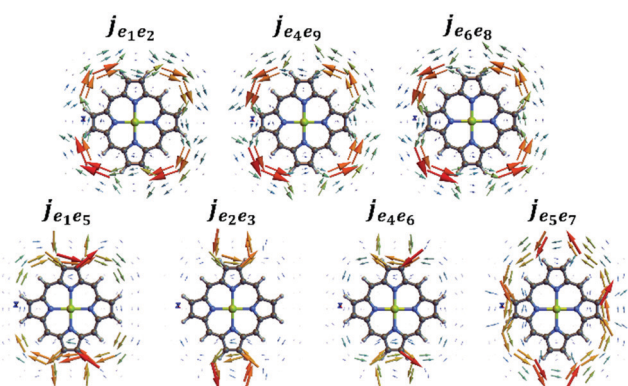


Fig. 2 The transition current density matrix elements in real space which generate the (quasi) ring currents. $j_{e_xe_y}$ is the transition current density between the e_x state and the e_y state.

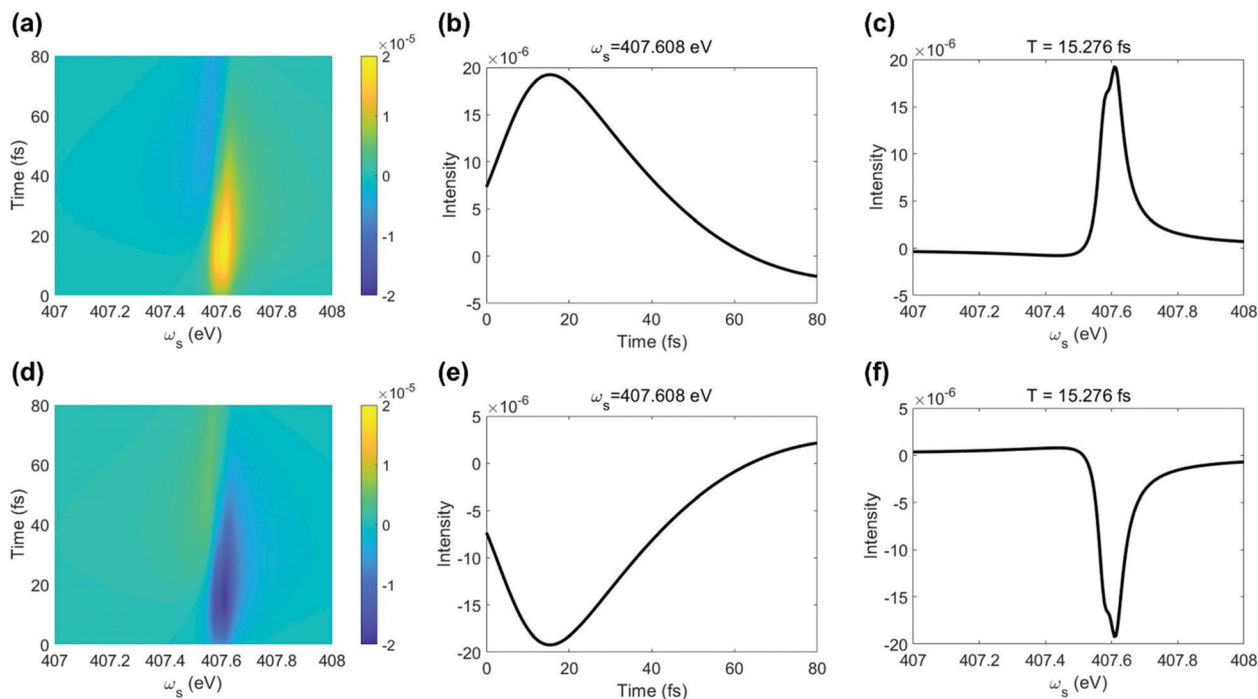


Fig. 3 Top: The TRCD signal calculated for the left (a–c) circularly polarized narrowband light pump. (b) shows the time variation of the TRCD signal along the maximum absolute value of the signal. (c) shows the TRCD signal vs. probe frequency ω_s . Bottom: (d–f) same but for the right polarized pump.

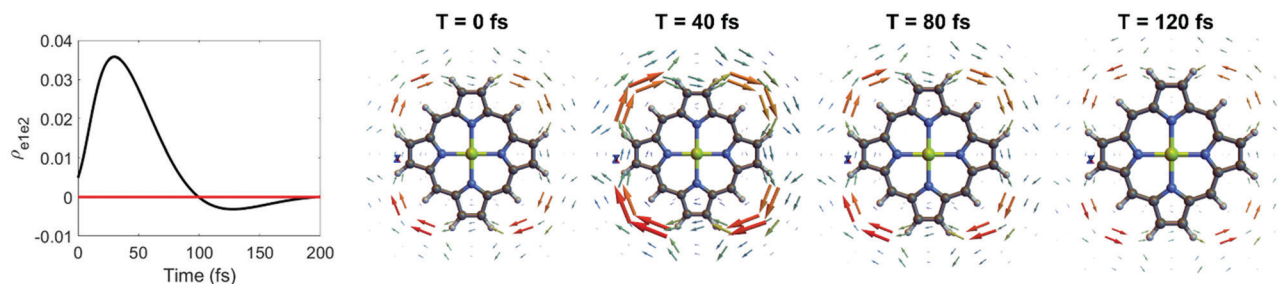


Fig. 4 The expectation value of the transition current density for (e_1e_2) coherence, $j_{e_1e_2}$, for several pump–probe waiting times, T .

asymmetry²⁹ as the ratio between the chiral contribution and the achiral background:

$$a_{CD}(\omega_s, T) = \frac{S_{abs}(\omega_s, T, L) - S_{abs}(\omega_s, T, R)}{1/2(S_{abs}(\omega_s, T, L) + S_{abs}(\omega_s, T, R))} \quad (10)$$

where S_{abs} indicates the absorption amplitude after interaction with the left or right circularly polarized X-ray probe pulse.

Note that the static X-ray absorption signal (XAS) cannot be used because it vanishes in the region of the spectrum where the transient appears. The asymmetry ratio would be ill-defined in most regions of the spectra. Thus, we use as a denominator of a_{CD} the value of the transient absorption in the spectral region of significant CD.

The asymmetry ratios a_{CD} at the N and Mg K-edge are shown in Fig. 5. The signals display unusually large asymmetry ratios (above 100%) compared to standard CD. This stems from the fact that no static signal (CD and XAS) exists in that spectral region, *i.e.* the transition from e_1 and e_2 to the core states is

made possible only by the actinic pump. Additionally, ring currents of opposite directions induce a significant difference in the transient absorption of the X-ray probe. We also observe that the asymmetry ratio is larger for Mg than for N, reaching a maximum of 164% for the former and 110% for the latter. This difference indicates that the Mg atom experiences a higher asymmetry, which can be assigned to the larger local magnetic field. The magnetic field created by the ring currents is the physical quantity breaking the parity of the molecular system and reaches its maximum at the ring center.

Fig. 6 depicts the TRCD signal for a broadband UV pump. It is generated by all possible coherences arising from the large bandwidth (1.0 eV), which covers the e_3 to e_9 valence states. The signal variation with time (Fig. 6b) is complex. The signal variation with ω_s (Fig. 6c) shows peaks near 405.3 and 405.7 eV, which correspond to transitions from the e_3 , e_5 , and e_7 valence excited states to the c_1 and c_2 core excited states. Again, the other core excitations make negligible contributions

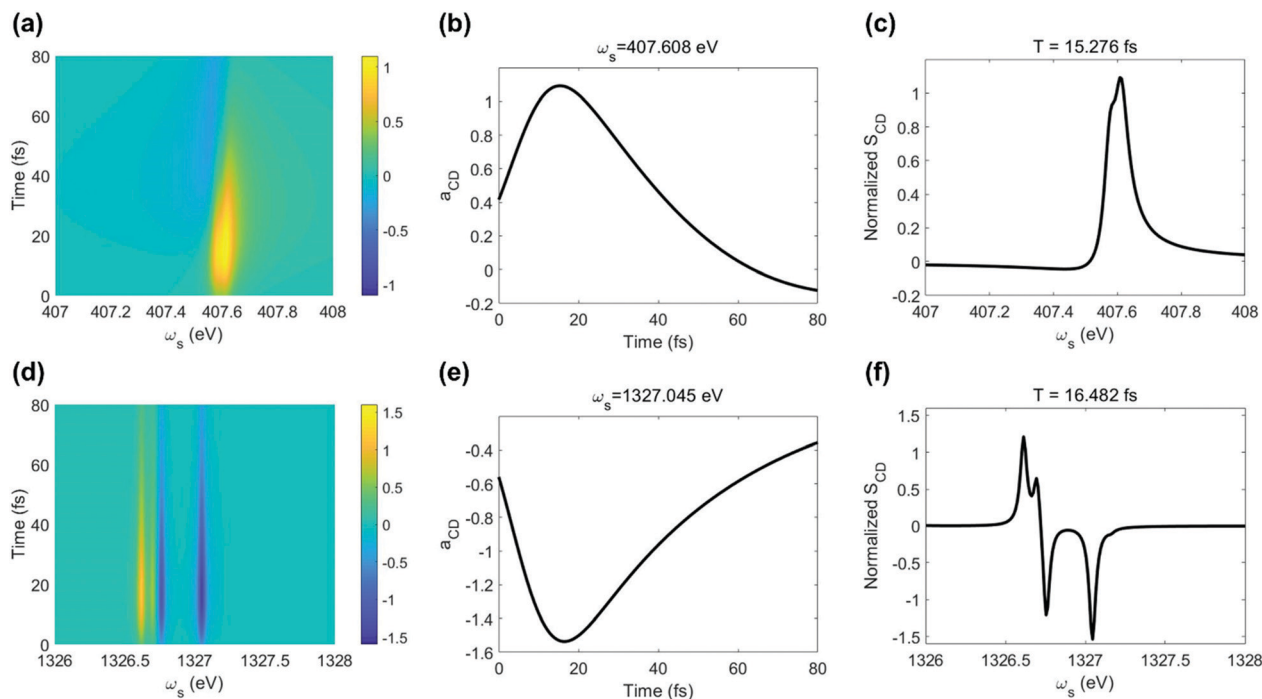


Fig. 5 Comparison of the TRCD asymmetry (a_{CD}), eqn (10), at the N (top, a–c) and Mg (bottom, d–f) K-edges. The asymmetry is larger when probing the magnesium than for the nitrogen atoms.

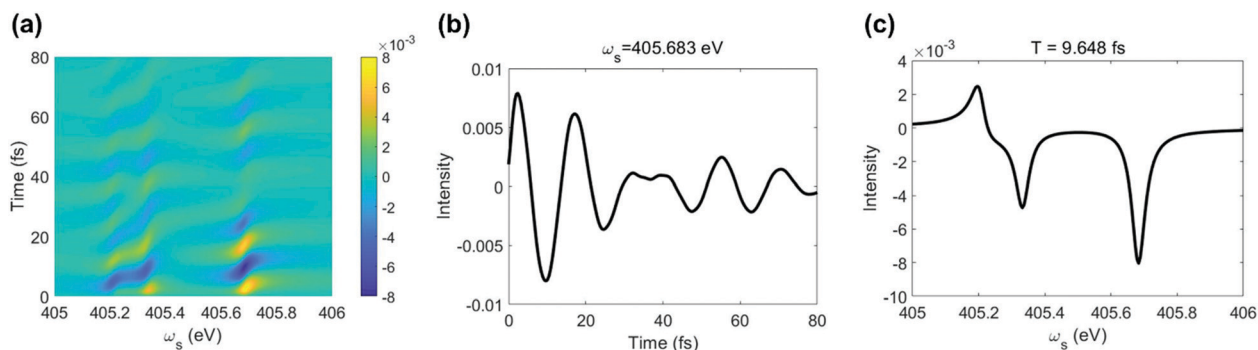


Fig. 6 The TRCD signal calculated for the left circularly polarized broadband light pump, where the central frequency was set to the transition energy between the ground and the 5th excited states. (b and c) show the TRCD signal *versus* time and probe frequency plots along the maximum absolute value of the TRCD signal, respectively.

to the signal due to their small transition current density. As shown in Fig. 6a, we find two coherences that contribute to the signal.

According to eqn (8), the signal is determined by $\rho_{ee'}(T)$ and the cross product, $\mathbf{j}_{e'c}(\mathbf{k}_s) \times \mathbf{j}_{ce'}(-\mathbf{k}_s)$. $\rho_{ee'}(T)$ values for possible coherences are shown in Fig. S4 (ESI†). It shows that $\rho_{e_3e_5}$, $\rho_{e_3e_7}$, and $\rho_{e_5e_7}$, which are the e_3e_5 , e_3e_7 , and e_5e_7 coherences, are dominant. This is because of the large transition dipole moments between the ground state and the e_3 , e_5 , and e_7 valence excited states.

The z component of the cross product $\mathbf{j}_{e'c}(\mathbf{k}_s) \times \mathbf{j}_{ce'}(-\mathbf{k}_s)$ is determined by the x component of $\mathbf{j}_{e'c}$ and the y component of $\mathbf{j}_{ce'}$ and *vice versa* (Table S3, ESI†). For the e_3 , e_5 , and e_7 valence excited states, the cross products $\mathbf{j}_{e_3c}(\mathbf{k}_s) \times \mathbf{j}_{ce_5}(-\mathbf{k}_s)$ and $\mathbf{j}_{e_3c}(\mathbf{k}_s) \times \mathbf{j}_{ce_7}(-\mathbf{k}_s)$ are larger than $\mathbf{j}_{e_5c}(\mathbf{k}_s) \times \mathbf{j}_{ce_7}(-\mathbf{k}_s)$ because

$\mathbf{j}_{ce_5}$ and $\mathbf{j}_{ce_7}$ both have a large y component but small x component, but $\mathbf{j}_{ce_3}$ has a large x component. Eventually, our signal mostly comes from the coherences e_3e_5 and e_3e_7 , which do not generate a ring current.

In the real system, the e_1 , e_3 , e_5 , and e_7 states are doubly degenerate, *i.e.* $\{e_1, e_1'\}, \dots, \{e_7, e_7'\}$ as reported by quantum calculations with high symmetry.^{33,36} Each coherence between degenerate states generates a ring current. By using a broadband pump, the TRCD signal probes multiple coherences which generate multiple ring currents.

It is clearer to use the TRCD signal to measure the ring current when it is accompanied by measurement of the induced magnetic field strength³⁷ because it can reflect the vorticity of the ring currents. The induced magnetic field at the center of

Table 1 The induced magnetic field strength (in Tesla) for different coherences, calculated at the center of Mg-porphyrin

The type of coherence	Induced magnetic field strength (T)		
	B_x	B_y	B_z
e_1e_2	0.0315	-0.0060	-0.2578
e_4e_9	-0.0170	0.0046	0.1349
e_6e_8	-0.0265	0.0049	0.2376
e_3e_5	-0.0030	0.0028	0.0185
e_3e_7	0.0001	-0.0007	~ 0

Mg-porphyrin ($x, y, z = 0$) can be calculated with the Biot-Savart law,²³

$$\mathbf{B}(x, y, z = 0) = -\frac{\mu_0}{4\pi} \iint \frac{\mathbf{j}(x, y, z) \times (-x\hat{x} - y\hat{y} - z\hat{z}) dx dy dz}{(x^2 + y^2 + z^2)^{3/2}} \quad (11)$$

where μ_0 refers to the vacuum permittivity, and $\hat{x}$, $\hat{y}$, and $\hat{z}$ are the unit vectors along the x , y , and z axis, respectively. The induced magnetic field strengths for the ring-current-generating coherences e_1e_2 , e_4e_9 , and e_6e_8 and the ring-current-non-generating coherences e_3e_5 and e_3e_7 are given in Table 1. The induced magnetic field strength along the z direction of the e_3e_5 and e_3e_7 coherences is 0.0185 and almost 0 T, respectively. In contrast, those of the e_1e_2 , e_4e_9 , and e_6e_8 coherences, -0.2578, 0.1349, and 0.2376 T, are around 10–20 times higher. The calculated magnetic field strengths are similar to a previous study,⁶ 0.159 T. However, note that the transition current density in eqn (11) does not reflect the small transition dipole

moment between the ground state and the dark states (e_4 , e_6 , e_8 , and e_9 states). The generation of the ring current $\mathbf{j}_{e_4e_9}$ and $\mathbf{j}_{e_6e_8}$ might be possible by relaxation from the other excited states to these optically dark states. Nevertheless, the measurement of the induced magnetic field helps to identify the ring current: the sign of the induced magnetic field marks the absolute direction of the ring current, where $\mathbf{j}_{e_1e_2}$ is a clockwise current while $\mathbf{j}_{e_4e_9}$ and $\mathbf{j}_{e_6e_8}$ are counterclockwise ring currents as shown in Fig. 2.

Fig. 7a and d show that the TRCD signals induced by a linearly polarized pump are about 1000 times smaller than the one induced by circular polarization. It indicates that circular polarization is an effective way of generating a ring current and induced magnetic field as suggested by the Manz group.⁶ It is apparent from the ladder diagram (Fig. 1b) that linear polarization along the x or y axis can excite only e_1 or e_2 from the ground state, and hence the cross product $\mathbf{j}_{e_1c}(\mathbf{k}_s) \times \mathbf{j}_{ce_1}(-\mathbf{k}_s)$ or $\mathbf{j}_{e_2c}(\mathbf{k}_s) \times \mathbf{j}_{ce_2}(-\mathbf{k}_s)$ becomes zero by definition. The ω_s vs. TRCD signal plot (Fig. 7c and f) shows only a single peak, compared to the double peak feature of the circular polarization, indicating that only the e_1 or e_2 state contributes to the TRCD signal. In our simulation, the x or y component of the transition dipole moment of e_1 and e_2 is not exactly zero, but around 1000 times smaller than their y or x component, making it 1000 times weaker than the TRCD signals induced by circular polarization.

Pumping with two pulses with x and y components is the same as pumping with a pulse oriented at 45° between x and y and can thus induce an e_1e_2 coherence that would give a

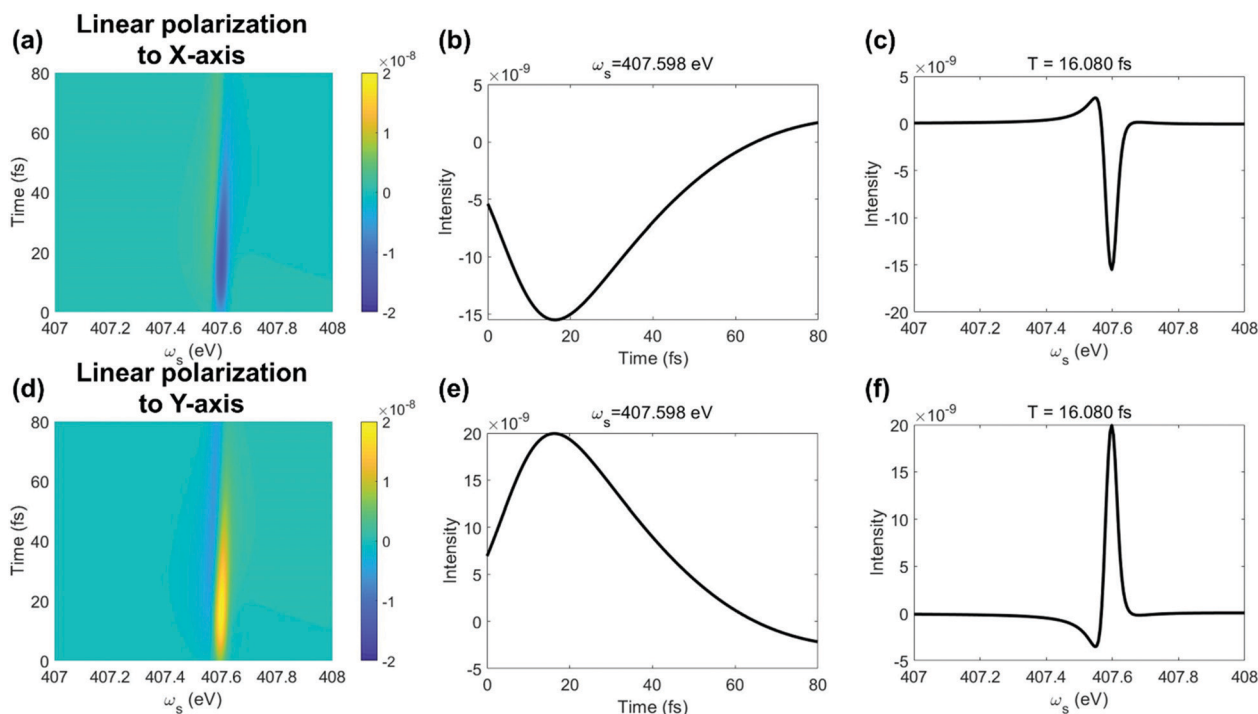


Fig. 7 The TRCD signal calculated for the linearly polarized light pump (a–c: linear polarization along the x -axis, d–f: linear polarization along the y -axis). (b and e) show the time variation of the TRCD signal along the maximum absolute value of the TRCD signal. (c and f) show the probe frequency ω_s versus TRCD signal.

non-vanishing signal. Indeed, TRCD is sensitive to coherences in general, of which ring currents are a special case. However, the coherences induced by an x - y pump scheme would not be a signature of a ring current and do not survive complete or partial rotational averaging. If the molecules are averaged around the probe (or pump) wavevectors, the pump + molecules have cylindrical symmetry, and an x - y polarized pump is totally equivalent to an x or y polarized pump. Ring currents in molecules are created by a transfer of angular momentum from the field to the matter³⁸ and an x - y linearly polarized pulse does not carry such momentum.

By the same argument, the TRCD signal is non-zero when coherences are present in the molecular system whether the system is aromatic or not, as long as the transition dipoles of the two transitions involved in the probe interaction are not pointing in the same direction. However, when a narrowband pump was used, an aromatic ring molecule would have a slow-decaying TRCD signal with larger magnitude while a non-aromatic ring molecule would have a fast-oscillating TRCD signal with much smaller magnitude because the cross product in eqn (8) is maximized for the degenerate states.

Conclusions

We have shown that time-resolved circular dichroism signals provide a direct measure of the magnitude and the direction of the electronic ring current. These measurements are simpler to interpret than photoelectron CD or high-harmonic-generation spectroscopy. The electronic ring current is generated by the coherent superposition of electronic states induced by circularly polarized light and is tracked by a time-delayed circularly polarized X-ray probe pulse. The signal is calculated using the minimal coupling Hamiltonian, which allows one to express it directly in terms of the relevant material quantity, transition current densities. The TRCD signals obtained from the left and right narrowband circularly polarized light pump have opposite signs, indicating that the signal is a direct signature of the ring current. The absolute value of the signal gives the magnitude of the ring current. The narrowband pump can selectively excite the doubly degenerate excited states to probe a specific ring current or the broadband pump can detect multiple coherences/ring currents at the same time.

X-rays allow one to study transient signals in regions where no static achiral background is present, leading to extremely large asymmetry ratios for such techniques. Additionally, X-rays can address different sites in the molecules. Here, we have focused on the amplitude of the TRCD signals for different atomic positions (at the center or on the ring); such sensitivity can also provide extra information for systems involving multiple rings with different atoms.

The strength of the induced magnetic field, calculated based on the Biot-Savart law, directly reflects the vorticity of an electronic coherence, which helps to identify a ring current and its absolute direction. Circular polarization is around 1000 times more sensitive than linear polarization to probe electronic coherences.

We expect that an aromatic and an anti-aromatic molecule will show the opposite TRCD signal under the same circularly polarized light pump. Hence, our direct approach to access the electronic coherences/ring currents opens a window to measure molecular aromaticity.³⁹ Furthermore, ring currents can be generated and probed by TRCD while a molecule is experiencing ultrafast nuclear dynamics, and can thus be a potential probe for photochemical ring opening or closure reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Monitoring Aromatic Ring-Currents in Mg-porphyrin by Time-Resolved Circular Dichroism

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1 Details of the time-resolved circular dichroism signal calculation

We start with the minimal coupling Hamiltonian, retaining only the current density term:

$$H_{\text{int}} = - \int d\mathbf{r} \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}, t) \quad (1)$$

where $\mathbf{j}(\mathbf{r})$ is transition current density and $\mathbf{A}(\mathbf{r}, t)$ is a vector potential of incoming pulse. The heterodyne-detected signal is defined as the change of the number of photons in a given time,

$$S(\Gamma) = \int dt \langle \dot{N}_s \rangle \quad (2)$$

where, Γ indicates the set of parameters, i.e. incoming pulses central frequencies, durations, etc.

$$\dot{N}_s = \frac{i}{\hbar} [H_{\text{int}}, N_s] = -\frac{i}{\hbar} \left[\int d\mathbf{r} \mathbf{j}(\mathbf{r}) \mathbf{A}(\mathbf{r}, t), a_s^\dagger a_s \right] \quad (3)$$

The vector potential $\mathbf{A}(\mathbf{r}, t)$ can be expressed as the following:

$$\mathbf{A}(\mathbf{r}, t) = \sqrt{\frac{\hbar}{2\epsilon_0\omega_s\Omega}} (a_s \boldsymbol{\varepsilon} e^{i(\mathbf{k}_s \cdot \mathbf{r} - \omega_s t)} + a_s^\dagger \boldsymbol{\varepsilon}^* e^{-i(\mathbf{k}_s \cdot \mathbf{r} - \omega_s t)}) \quad (4)$$

where $\boldsymbol{\varepsilon}$ is the electric field polarization vectors. Hence, it gives

$$\dot{N}_s = -\frac{i}{\hbar} \int d\mathbf{r} \mathbf{j}(\mathbf{r}) \cdot [\mathbf{A}(\mathbf{r}, t), a_s^\dagger a_s] = -\frac{2}{\hbar} \text{Im} \int d\mathbf{r} \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}^*(\mathbf{r}, t) \quad (5)$$

Therefore, the heterodyne-detected signal is

$$S(\Gamma) = -\frac{2}{\hbar} \text{Im} \int d\mathbf{r} dt \langle \mathbf{j}(\mathbf{r}, t) \cdot \mathbf{A}^*(\mathbf{r}, t) \rangle \quad (6)$$

The heterodyne-detected signal for Fig. S1 corresponds to

$$S(\Gamma) = -\frac{2}{\hbar} \text{Im} \int d\mathbf{r} dt d\mathbf{r}_3 dt_3 d\mathbf{r}_2 dt_2 d\mathbf{r}_1 dt_1 \left(-\frac{i}{\hbar} \right)^3 \langle j_{\text{left}}(\mathbf{r}, t) j_{\text{left}}^\dagger(\mathbf{r}_3, t_3) j_{\text{right}}^\dagger(\mathbf{r}_2, t_2) j_{\text{right}}(\mathbf{r}_1, t_1) \rangle A_s^*(\mathbf{r}, t) A_s(\mathbf{r}_3, t_3) A_{\text{pu}}(\mathbf{r}_2, t_2) A_{\text{pu}}^*(\mathbf{r}_1, t_1) \quad (7)$$

The A_s and A_{pu} is the vector potential of a probe and pump pulse respectively. The subscript left and right indicates the Liouville space superoperators defined by $O_{\text{left}}\rho = O\rho$ and $O_{\text{right}}\rho = \rho O$. Upon expanding to first order in the probe and taking the difference between left and right polarization of the probe, we get

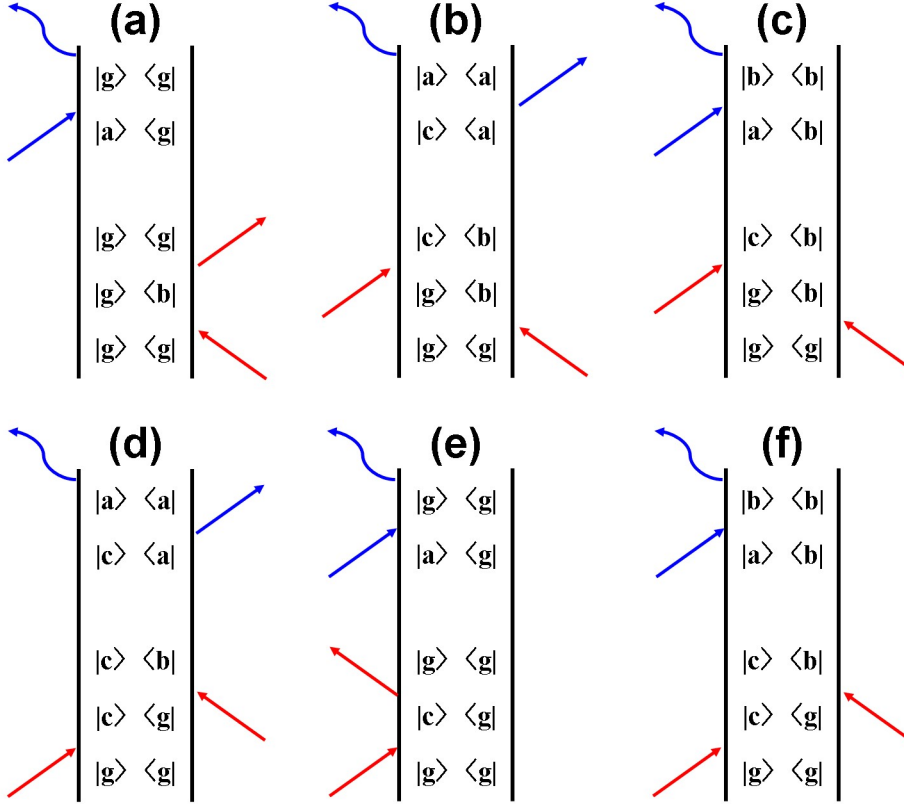


Figure. S 1: Possible pump-probe ladder diagrams. t_1 , t_2 , and t_3 refer to the time interval between interaction. Red and blue arrow indicates UV pump and X-ray probe interaction, respectively.

$$\begin{aligned}
S_{jj}(\Gamma) &= -\frac{2}{\hbar} \text{Im} \int d\mathbf{r} d\mathbf{t} d\mathbf{r}_1 d\mathbf{t}_1 \left(-\frac{i}{\hbar} \right) \left[\langle j_{\text{left}}(\mathbf{r}, t) j_{\text{left}}^\dagger(\mathbf{r}_1, t - t_1) \rangle A_s^*(\mathbf{r}, t) A_s(\mathbf{r}_1, t - t_1) \right. \\
&\quad \left. - \langle j_{\text{left}}(\mathbf{r}, t) j_{\text{right}}^\dagger(\mathbf{r}_1, t - t_1) \rangle A_s^*(\mathbf{r}, t) A_s(\mathbf{r}_1, t - t_1) \right] \\
&= \frac{2}{\hbar^2} \text{Re} \int d\mathbf{r} d\mathbf{t} d\mathbf{r}_1 d\mathbf{t}_1 \left[\langle \langle j(\mathbf{r}) | \mathcal{G}(t_1) j_{\text{left}}^\dagger(\mathbf{r}_1) | \rho(t - t_1) \rangle \rangle A_s^*(\mathbf{r}, t) A_s(\mathbf{r}_1, t - t_1) \right. \\
&\quad \left. - \langle \langle j(\mathbf{r}) | \mathcal{G}(t_1) j_{\text{right}}^\dagger(\mathbf{r}_1) | \rho(t - t_1) \rangle \rangle A_s^*(\mathbf{r}, t) A_s(\mathbf{r}_1, t - t_1) \right] \\
&= \frac{2}{\hbar^2} \text{Re} \int d\mathbf{r} d\mathbf{t} d\mathbf{r}_1 d\mathbf{t}_1 \left[\langle \langle j(\mathbf{r}) | \mathcal{G}(t_1) j_{\text{left}}^\dagger(\mathbf{r}_1) | \rho(t - t_1) \rangle \rangle \right. \\
&\quad \left. - \langle \langle j(\mathbf{r}) | \mathcal{G}(t_1) j_{\text{right}}^\dagger(\mathbf{r}_1) | \rho(t - t_1) \rangle \rangle \right] \left(\epsilon_L^* \epsilon_L - \epsilon_R^* \epsilon_R \right) A_s^*(\mathbf{r}, t) A_s(\mathbf{r}_1, t - t_1) e^{-ik_s r + ik_s r_1} e^{i\omega_s t_1}
\end{aligned}
\tag{8}$$

Using that $\varepsilon_L^{a*} \varepsilon_L^b - \varepsilon_R^{a*} \varepsilon_R^b = (-i)\varepsilon_{abz}$, where ε_{abz} is a Levi-Civita symbol and summing over electronic eigenstates, we get

$$S_{\text{CD}} = \frac{2}{\hbar^2} \text{Im} \int d\mathbf{r} d\mathbf{t} d\mathbf{r}_1 d\mathbf{t}_1 \varepsilon_{abz} [\langle \langle j^a(\mathbf{r}) | \mathcal{G}(t_1) j_{\text{left}}^{\dagger b}(\mathbf{r}_1) | \rho(t-t_1) \rangle \rangle - \langle \langle j^a(\mathbf{r}) | \mathcal{G}(t_1) j_{\text{right}}^{\dagger b}(\mathbf{r}_1) | \rho(t-t_1) \rangle \rangle] \mathbf{A}_s^*(\mathbf{r}, t) \mathbf{A}_s(\mathbf{r}_1, t-t_1) e^{-i\mathbf{k}_s \mathbf{r} + i\mathbf{k}_s \mathbf{r}_1} e^{i\omega_s t_1} \quad (9)$$

and

$$\langle \langle ab | j_L - j_R | cd \rangle \rangle = j_{ac} \delta_{bd} - j_{bd} \delta_{ac} \quad (10)$$

then,

$$\begin{aligned} S_{\text{CD}} &= \frac{2}{\hbar^2} \text{Im} \int d\mathbf{r} d\mathbf{t} d\mathbf{r}_1 d\mathbf{t}_1 [\langle \langle \mathbf{j}(\mathbf{r}) \times | \mathcal{G}(t_1) j_-^\dagger(\mathbf{r}_1) | \rho(t-t_1) \rangle \rangle] \mathbf{A}_s^*(\mathbf{r}, t) \mathbf{A}_s(\mathbf{r}_1, t-t_1) e^{-i\mathbf{k}_s \mathbf{r} + i\mathbf{k}_s \mathbf{r}_1} e^{i\omega_s t_1} \\ &= \frac{2}{\hbar^2} \text{Im} \int d\mathbf{t} d\mathbf{t}_1 [\langle \langle \mathbf{j}(\mathbf{k}_s) \times | \mathcal{G}(t_1) j_-^\dagger(-\mathbf{k}_s) | \rho(t-t_1) \rangle \rangle] \mathbf{A}_s^*(t) \mathbf{A}_s(t-t_1) e^{i\omega_s t_1} \\ &= \frac{2}{\hbar^2} \text{Im} \sum_{abc} \int d\mathbf{t} d\mathbf{t}_1 (j_{ba}(\mathbf{k}_s) \times) e^{-i\omega_{ab} t_1 - \Gamma_{ab} t_1} [j_{ac}^\dagger(-\mathbf{k}_s) \delta_{bd} - j_{bd}^\dagger(-\mathbf{k}_s) \delta_{ac}] \rho_{cd}(t-t_1) \mathbf{A}_s^*(t) \mathbf{A}_s(t-t_1) e^{i\omega_s t_1} \end{aligned} \quad (11)$$

where j_- denotes the Liouville space current density superoperator defined by $j_- \rho = j\rho - \rho j$.

$$\begin{aligned} S_{\text{CD}} &= \frac{2}{\hbar^2} \text{Im} \sum_{abc} \int d\mathbf{t} d\mathbf{t}_1 [j_{ba}(\mathbf{k}_s) \times j_{ac}^\dagger(-\mathbf{k}_s) e^{i(\omega_s - \omega_{ab})t_1 - \Gamma_{ab} t_1} \rho_{cb}(t-t_1) \\ &\quad - j_{ba}(\mathbf{k}_s) \times j_{bc}^\dagger(-\mathbf{k}_s) e^{i(\omega_s - \omega_{ab})t_1 - \Gamma_{ab} t_1} \rho_{ac}(t-t_1)] \mathbf{A}_s^*(t) \mathbf{A}_s(t-t_1) \end{aligned} \quad (12)$$

Rearranging the sums to factorized out the density matrix after the pump, we get

$$S_{\text{CD}}(\mathbf{k}_s, \omega_s) = \frac{2}{\hbar^2} \text{Im} \sum_{abc} \int d\mathbf{t} d\mathbf{t}_1 \mathbf{A}_s^*(t) \mathbf{A}_s(t-t_1) \rho_{cb}(t-t_1) [j_{ba}(\mathbf{k}_s) \times j_{ac}^\dagger(-\mathbf{k}_s) e^{i(\omega_s - \omega_{ab})t_1 - \Gamma_{ab} t_1} - j_{ac}(\mathbf{k}_s) \times j_{ab}^\dagger(-\mathbf{k}_s) e^{i(\omega_s - \omega_{ca})t_1 - \Gamma_{ca} t_1}] \quad (13)$$

In the impulsive limit, $\mathbf{A}_s(t) = \delta(t-T)\mathbf{A}_s$, $\mathbf{A}_s(t-t_1) = \delta(t-t_1-T)\mathbf{A}_s$, where $t \rightarrow T$, and $t_1 \rightarrow 0$.

We now express explicitly $\rho_{cb}(T)$. At second order in the pump interaction (Fig S4), we have

$$\begin{aligned} \rho_{cb}(T) &= \langle \langle cb | \rho(T) \rangle \rangle \\ &= -\left(\frac{-i}{\hbar}\right)^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{t}_1 d\mathbf{t}_2 \langle \langle cb | j_-(\mathbf{r}_2, t_2) j_-(\mathbf{r}_1, t_1) | \rho(T-t_1-t_2) \rangle \rangle \mathbf{A}_{\text{pu}}^*(\mathbf{r}_2, T-t_2) \mathbf{A}_{\text{pu}}(\mathbf{r}_1, T-t_2-t_1) \\ &= -\left(\frac{-i}{\hbar}\right)^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{t}_1 d\mathbf{t}_2 \left(\langle \langle cb | \mathcal{G}(t_2) j_{\text{right}}(\mathbf{r}_2) \mathcal{G}(t_1) j_{\text{left}}^\dagger(\mathbf{r}_1) | \rho(t_0) \rangle \rangle \mathbf{A}_{\text{pu}}^*(\mathbf{r}_2, T-t_2) \mathbf{A}_{\text{pu}}(\mathbf{r}_1, T-t_2-t_1) \right. \\ &\quad \left. + \langle \langle cb | \mathcal{G}(t_2) j_{\text{left}}^\dagger(\mathbf{r}_2) \mathcal{G}(t_1) j_{\text{right}}(\mathbf{r}_1) | \rho(t_0) \rangle \rangle \mathbf{A}_{\text{pu}}(\mathbf{r}_2, T-t_2) \mathbf{A}_{\text{pu}}^*(\mathbf{r}_1, T-t_2-t_1) \right) \end{aligned} \quad (14)$$

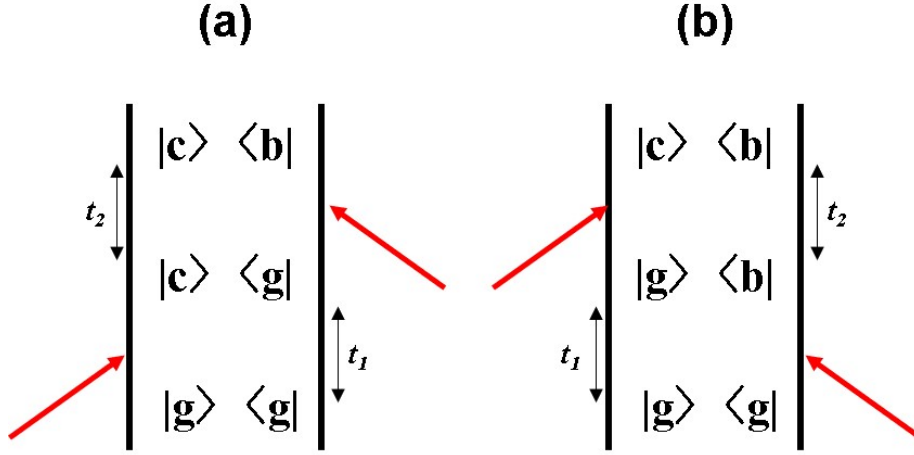


Figure. S 2: Ladder diagrams for pump interaction. t_1 and t_2 , refer to the time interval between two pump interactions.

Since, $\rho(t_0) = |gg\rangle\rangle$

$$\begin{aligned}
 \rho_{cb}(T) &= \left(\frac{1}{\hbar}\right)^2 \int d\mathbf{r}_1 d\mathbf{r}_2 dt_1 dt_2 \left(\mathcal{G}_{cb,cb}(t_2) j_{bg}(\mathbf{r}_2) \mathcal{G}_{cg,cg}(t_1) j_{cg}^\dagger(\mathbf{r}_1) A_{pu}^*(\mathbf{r}_2, T-t_2) A_{pu}(\mathbf{r}_1, T-t_2-t_1) \right. \\
 &\quad \left. + \mathcal{G}_{cb,cb}(t_2) j_{cg}^\dagger(\mathbf{r}_2) \mathcal{G}_{gb,gb}(t_1) j_{bg}(\mathbf{r}_1) A_{pu}(\mathbf{r}_2, T-t_2) A_{pu}^*(\mathbf{r}_1, T-t_2-t_1) \right) \\
 &= \frac{1}{\hbar^2} \int dt_1 dt_2 \left(e^{-i\omega_{cb}t_2 - \Gamma_{cb}t_2} e^{-i\omega_{cg}t_1 - \Gamma_{cg}t_1} j_{bg}(\mathbf{k}_{pu}) j_{cg}^\dagger(-\mathbf{k}_{pu}) A_{pu}^*(T-t_2) A_{pu}(T-t_2-t_1) \right. \\
 &\quad \left. + e^{-i\omega_{cb}t_2 - \Gamma_{cb}t_2} e^{-i\omega_{gb}t_1 - \Gamma_{gb}t_1} j_{cg}^\dagger(-\mathbf{k}_{pu}) j_{bg}(\mathbf{k}_{pu}) A_{pu}(T-t_2) A_{pu}^*(T-t_2-t_1) \right) \quad (15)
 \end{aligned}$$

In the impulsive limit, $A_{pu}(t) = \delta(t)A_{pu}$, where $t_2 \rightarrow T$, and $t_1 \rightarrow 0$. The Fourier transform of pump pulse in time-domain to frequency domain gives,

$$A_{pu}(T-t_1) = \int \frac{d\omega_1}{2\pi} A_{pu}(\omega_1) e^{-i\omega(T-t_1)} \quad (16)$$

and

$$\int_0^\infty dt_2 e^{i(\omega_1 - \omega_2 - \omega_{cb}t_2 - \Gamma_{cb}t_2)} = \frac{i}{\omega_1 - \omega_2 - \omega_{cb} + i\Gamma_{cb}} \quad (17)$$

Hence, the density matrix at waiting time T becomes,

$$\rho_{cb}(T) = -\frac{1}{\hbar^2} \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} A_{\text{pu}}(\omega_1) A_{\text{pu}}(\omega_2) \left[\frac{\mathbf{j}_{bg}(\mathbf{k}_{\text{pu}}) \cdot \boldsymbol{\varepsilon}_{\text{pu}}^* \cdot \mathbf{j}_{cg}^{\dagger}(-\mathbf{k}_{\text{pu}}) \cdot \boldsymbol{\varepsilon}_{\text{pu}} e^{i(\omega_2 - \omega_1)T}}{(\omega_1 - \omega_2 - \omega_{cb} + i\Gamma_{cb})(\omega_1 - \omega_{cg} + i\Gamma_{cg})} + \frac{\mathbf{j}_{cg}^{\dagger}(-\mathbf{k}_{\text{pu}}) \cdot \boldsymbol{\varepsilon}_{\text{pu}} \cdot \mathbf{j}_{bg}(\mathbf{k}_{\text{pu}}) \cdot \boldsymbol{\varepsilon}_{\text{pu}}^* e^{-i(\omega_2 - \omega_1)T}}{(-\omega_1 + \omega_2 - \omega_{cb} + i\Gamma_{cb})(-\omega_1 - \omega_{gb} + i\Gamma_{gb})} \right] \quad (18)$$

Likewise, the final TRCD signal becomes,

$$S_{\text{CD}}(\omega_s, T) = \frac{2}{\hbar^2} \frac{1}{(2\pi)^2} N \text{Re} \sum_{abc} A_s^*(\omega_s) A_s(\omega_s) \rho_{cb}(T) \left[\frac{\mathbf{j}_{ba}(\mathbf{k}_s) \times \mathbf{j}_{ac}^{\dagger}(-\mathbf{k}_s)}{\omega_s - \omega_{ab} + i\Gamma_{ab}} - \frac{\mathbf{j}_{ac}(\mathbf{k}_s) \times \mathbf{j}_{ab}^{\dagger}(-\mathbf{k}_s)}{-\omega_s - \omega_{ca} + i\Gamma_{ca}} \right] \quad (19)$$

Finally, substituting a , b , and c into c , e' , and e , respectively, gives the final expression in the manuscript.

2 Quantum simulation results

We compared our quantum calculations with previous work of Rubio [1] which performed CASSCF calculations within the same active space (13o/18e) for the electronic structure calculation of the Mg-porphyrin. To that end, we computed transition energies (Table S1 and S2) and transition dipole moment (Fig. S3) of the Mg-porphyrin calculated at the CASSCF (13o/18e) level with C_1 and D_{2h} symmetry option (note that the highest symmetry option in MOLPRO is D_{2h}). By comparing the orbital configuration of each excited state of the active orbitals, we assigned our e_1, e_3, e_5 , and e_7 states to e_1 to e_4 states (Q band to N band) of Rubio’s work and those of D_{2h} symmetry. The e_1, e_3, e_5 , and e_7 states are originally doubly degenerate, however, they might split into several non-degenerate states due to the loss of symmetry [1, 2]: for example, the Q bands split into e_1 and e_2 states. Discrepancies of the computed transition energies compared to experimental data are due to the lack of dynamics correlation in CASSCF. However, our computation matches the results of the CASSCF calculation of Rubio [1] in terms of transition energies and orbital configurations. Moreover, the square of transition dipole moment with D_{2h} symmetry shows the same trend ($e_1 < e_3, e_3 > e_5$, and $e_5 < e_7$). The small deviation from Rubio’s work mainly originates from the different basis set and since the oscillator strength was calculated with CASPT2 in that study. It is also consistent with experiment that the absorption of e_1 is very weak and e_3 shows the most intense absorption [3].

	CASSCF (13o/20e) with C_1 symmetry				Rubio’s work ⁵ : CASSCF (13o/18e)			Experiment ¹
	Transition Energy	Square of the transition dipole moment, μ^2	Transition dipole moment direction	Main orbital configuration (with D_{2h} notation)	Transition Energy	Oscillator Strength	Main orbital configuration (D_{4h})	Transition Energy
e_1	3.125	0.199	x	$6B_{1u} \rightarrow 4B_{2g} (B_{3u})$ $2A_u \rightarrow 4B_{3g} (B_{3u})$	3.05	0.008	$4a_{2u} \rightarrow 4e_g$ $1a_{1u} \rightarrow 4e_g$	2.14
e_2	3.157	0.748	y	$6B_{1u} \rightarrow 4B_{3g} (B_{2u})$ $2A_u \rightarrow 4B_{2g} (B_{2u})$				
e_3	5.051	14.054	x	$6B_{1u} \rightarrow 4B_{2g} (B_{3u})$ $2A_u \rightarrow 4B_{3g} (B_{3u})$ $4B_{1u} \rightarrow 4B_{2g} (B_{3u})$	4.95	0.923	$4a_{2u} \rightarrow 4e_g$ $1a_{1u} \rightarrow 4e_g$ $3a_{2u} \rightarrow 4e_g$	3.18
e_4	5.274	0.000	y	$3B_{3g} \rightarrow 4B_{2g} (B_{1g})$				
e_5	5.400	20.418	y	$6B_{1u} \rightarrow 4B_{3g} (B_{2u})$ $2A_u \rightarrow 4B_{2g} (B_{2u})$	5.28	0.200	$2b_{2u} \rightarrow 4e_g$	3.40
e_6	5.492	0.000	x	$3B_{2g} \rightarrow 4B_{2g} (A_g)$				
e_7	5.527	6.413	x	$4B_{1u} \rightarrow 4B_{2g} (B_{3u})$	5.83	0.379	$3a_{2u} \rightarrow 4e_g$	3.81
e_8	5.664	0.000	y	$3B_{2g} \rightarrow 4B_{3g} (B_{1g})$				
e_9	5.793	0.000	x	$3B_{3g} \rightarrow 4B_{3g} (A_g)$				

Table S 1: Comparison of transition energies (eV), transition dipole moment (a.u.), main orbital configuration of Mg-porphyrin between this study (with C_1 symmetry), Rubio’s work [1] and experimental results [3]. The main orbital configuration of C_1 symmetry was converted to the orbital notations of D_{2h} symmetry for convenience.

	CASSCF (13o/20e) with D _{2h} symmetry				Rubio's work ⁵ : CASSCF (13o/18e)			Experiment ¹
	Transition Energy	Square of the transition dipole moment, μ ²	Transition dipole moment direction	Main orbital configuration (Wavefunction symmetry)	Transition Energy	Oscillator Strength	Main orbital configuration	Transition Energy
<i>e</i> ₁	2.869	0.493	x	2A _u → 4B _{3g} (B _{3u}) 6B _{1u} → 4B _{2g} (B _{3u})	3.05	0.008	4a _{2u} → 4e _g 1a _{1u} → 4e _g	2.14
<i>e</i> ₁ '	2.869	0.493	y	2A _u → 4B _{2g} (B _{2u}) 6B _{1u} → 4B _{3g} (B _{2u})				
<i>e</i> ₂	4.836	16.945	x	6B _{1u} → 4B _{2g} (B _{3u}) 2A _u → 4B _{3g} (B _{3u}) 4B _{1u} → 4B _{2g} (B _{3u})	4.95	0.923	4a _{2u} → 4e _g 1a _{1u} → 4e _g 3a _{2u} → 4e _g	3.18
<i>e</i> ₂ '	4.836	16.945	y	6B _{1u} → 4B _{3g} (B _{2u}) 2A _u → 4B _{2g} (B _{2u}) 4B _{1u} → 4B _{3g} (B _{2u})				
<i>e</i> ₃	5.281	1.417	x	5B _{1u} → 4B _{2g} (B _{3u})	5.28	0.200	2b _{2u} → 4e _g	3.40
<i>e</i> ₃ '	5.281	1.417	y	5B _{1u} → 4B _{3g} (B _{2u})				
<i>e</i> ₄	5.815	2.521	x	4B _{1u} → 4B _{2g} (B _{3u})	5.83	0.379	3a _{2u} → 4e _g	3.81
<i>e</i> ₄ '	5.815	2.521	y	4B _{1u} → 4B _{3g} (B _{2u})				

Table S 2: Comparison of transition energies (eV), transition dipole moment (a.u.), main orbital configuration of Mg-porphyrin between this study (with D_{2h} symmetry), Rubio's work [1] and experimental results [3].

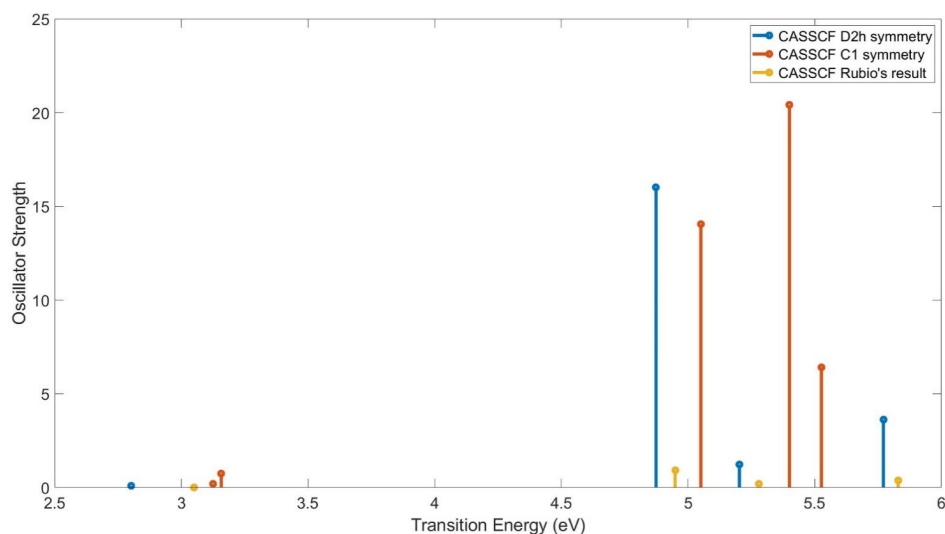


Figure. S 3: Stick spectra of the oscillator strength for the valence excitations from the ground state. Blue: CASSCF calculation with D_{2h} symmetry, Red: CASSCF calculation with C_1 symmetry, Yellow: CASSCF result [1].

3 Time-dependent density matrix elements and Average transition current density

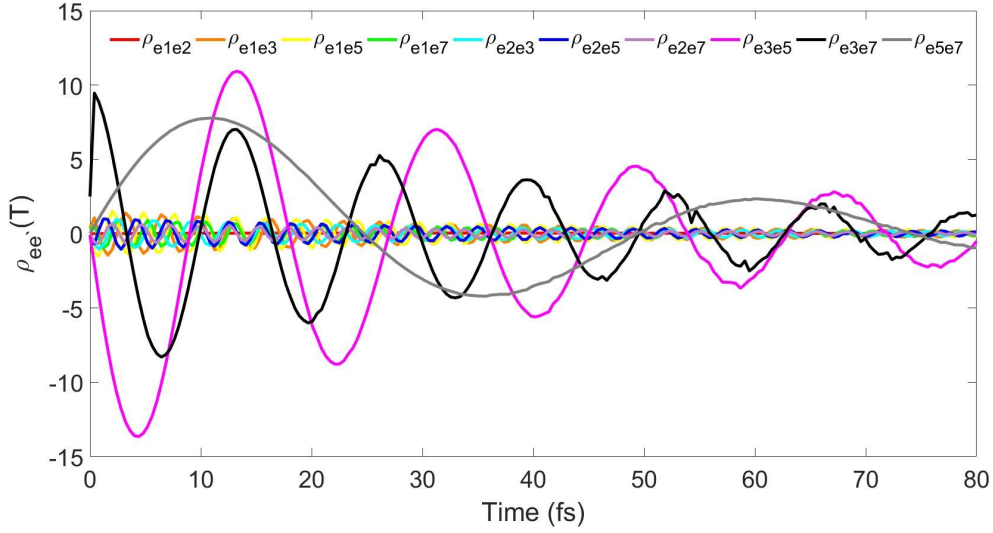


Figure. S 4: The time-dependent density matrix for various coherences of valence excited states. The density matrix originating only from e_1 , e_2 , e_3 , e_5 , and e_7 are shown.

$\dot{j}_{ab}$	c_1		c_2	
	x	y	x	y
e_3	-7.137	2.086	-7.137	2.087
e_5	-0.300	-4.448	-0.300	-4.448
e_7	0.245	-5.231	0.245	-5.231

Table S 3: The average transition current density value for the transition from e_3 , e_5 , and e_7 valence state to c_1 and c_2 core states in the real space (x and y component are separately shown, Unit: $10^{-7} e/\text{bohr}^3$), where e is the electron charge.

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