Optical activity from exciton Aharonov-Bohm effect: a Floquet engineering approach

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Abstract

Floquet engineering is a convenient strategy to induce nonequilibrium phenomena in molecular and solid-state systems, or to dramatically alter the physicochemical properties of matter bypassing costly and time-consuming synthetic modifications. In this article, we theoretically demonstrate that an originally achiral molecular system can exhibit nonzero circular dichroism (CD) when it is driven with elliptically polarized light. More specifically, we consider an isotropic ensemble of small cyclic molecular aggregates in solution whose local low-frequency vibrational modes are driven by a continuous-wave infrared pump. We attribute the origin of the nonzero CD to time-reversal symmetry breaking due to an excitonic Aharonov-Bohm (AB) phase arising from laser-driving and coherent interchromophoric exciton hopping. The obtained Floquet-engineered excitonic AB phases are far more tunable than their analogous electronic AB phases in the nanoscale, highlighting a virtually unexplored potential that excitonic AB phases have in the coherent control of molecular processes and simultaneously introducing new analogues of magneto-optical effects in molecular systems which bypass the use of strong magnetic fields.
Introduction

Molecular enantiomers exhibit slightly different interactions with right and left-handed circular polarized light (RCP, LCP) fields. There are two important consequences of this effect: non-racemic samples exhibit finite circular dichroism (CD) (difference in absorption rate of RCP and LCP fields) and finite optical rotation (OR) (rotation of the plane of linearly polarized light). The phenomena of CD and OR are intimately related by Kramers-Kronig relations and are collectively known as “optical activity”\(^1\). CD and OR are well-established spectroscopic techniques to probe enantiomeric excess in chemical samples. Interestingly, optical activity is not restricted to samples involving chiral molecules, but can also arise in any material which interacts with a static magnetic field that is parallel to the propagation direction of light. To distinguish the optical activity due to magnetic field from that due to the breakdown of molecular inversion symmetry, the latter so-called magneto-optical (MO) effects are known as magnetic CD (MCD) and magnetic OR (MOR) or Faraday effect, respectively. MCD is an important spectroscopic technique that allows to resolve electronic transitions in congested absorption bands\(^2\), while MOR is a phenomenon that is routinely exploited in the fabrication of optical devices such as isolators and circulators\(^2 - 4\).

The fundamental origin of MO effects is the breakdown of time-reversal symmetry (TRS). It is thus reasonable that analogous effects to MO ones could arise from replacing a static magnetic field with time-varying electric fields; we shall hearefter term them pseudo-MO effects. In molecular spectroscopy, these effects have been long recognized since the pioneering works of Atkins and Miller\(^5\). More recently, within the context of topological photonics and nonreciprocal media, much attention has been placed in exploiting time-varying modulation of material permittivities as a way to generate synthetic gauge (“pseudo-magnetic”) fields, therefore circumventing magnetic field strengths that could be prohibitive in general experimental setups or difficult to integrate in optoelectronic devices. In fact, photonic versions of the Aharonov-Bohm (AB) effect\(^6\) and quantum Hall systems\(^7 - 9\) have been successfully demonstrated in arrays of RLC microresonators\(^10 - 11\).
breaking is the realization of AB phases that differ from 0 or $\pi \mod 2\pi$. This is astutely realized in \cite{12} by driving resonators in adjacent unit cells so that there is a large phase lag between them, a feature that is facilitated by the relatively big mesoscopic lengthscales of the experimental system. Thus, it is not obvious \textit{a priori} whether such strategy would be feasible in the recreation of pseudo-magnetic fields in the molecular aggregates or in general nanoscale situations, especially considering the lengthscale mismatch between the typical intermolecular distance and an optical wavelength of the driving field. However, as we shall show in the present article, such mismatch can be compensated by invoking rings of coherently coupled anisotropic nanoscale dipoles interacting with an elliptically polarized laser light such that different sites interact with different polarizations of the laser and consequently pick up distinct phases from the field.

In this paper, we present a theoretical proof of principle of the possibility of inducing synthetic gauge fields in the excitonic degrees of freedom of small cyclic molecular aggregates. In particular, we design a setup consisting of an isotropically averaged ensemble of molecular homotetramers where each of the sites has an internal vibronic structure with low-frequency (e.g., vibrational) transitions that are driven by a resonant electric field. Owing to the periodicity of the laser-driving, we employ Floquet theory\cite{13,14} to calculate the spectral properties of the laser-driven system according to a recently developed methodology\cite{15}. These Floquet engineering concepts are complementary to recent efforts using strong magnetic fields to dramatically alter the vibronic structure and consequently the optical properties of molecular aggregates, such as in the excited vibronic structure of light harvesting complexes in cryptophyte algae\cite{16}, as well as to the design of topologically nontrivial phases in organic excitonic systems\cite{17}. In particular, our study highlights the simplicity with which large values of excitonic AB phases can be obtained in nanoscale systems (as shown below, with weak laser intensities), in contrast with the difficulty associated with the giant magnetic fields that must be present for a nanoring to generate similarly large values of electronic AB phases. Hence, our results suggest much flexibility on the use of elliptically polarized light in the realization
of excitonic AB phases that could control a variety of charge and energy transfer processes in molecular aggregates, as well as manipulate the spectroscopic properties of the latter. While excitonic AB phases that depend on the separation between electron and hole have been studied in inorganic Wannier exciton systems, similar phases in Frenkel organic exciton systems are far underexplored and constitute an interesting frontier in physical chemistry.

Theoretical Formalism

![Diagram](image)

**Figure 1: Anthracene monomer.** (a) Molecular structure and dipole moment vector corresponding to the $S_0 \rightarrow S_1$ transition. (b) Simplified displaced harmonic oscillator spectrum of anthracene along low-frequency vibrational mode ($\omega_{\text{vib}} = 385 \text{ cm}^{-1}$). Here, $\omega_e = 27,695 \text{ cm}^{-1}$ is the 0-0’ electronic transition frequency and $D = 0.31$ is the Huang-Rhys parameter for vibronic coupling. (c) In this work, we will simplify the spectrum in (b) with a three-level model.

**Definition of excitonic model**

The building block of our molecular aggregates is an anthracene molecule, depicted in Figure 1. We shall only be concerned with its $S_0 \rightarrow S_1$ electronic transition (with 0-0’ frequency $\omega_e = 27,695 \text{ cm}^{-1}$) which is coupled to a low-frequency $a_g$ mode $\omega_{\text{vib}} = 385 \text{ cm}^{-1}$; the Huang-Rhys...
Figure 2: Realization of excitonic Aharonov-Bohm effect (ABE) in cyclic molecular aggregates via Floquet engineering with elliptically polarized light. (a) Example geometry of an anthracene homotetramer where relative orientations ($\theta_1$, $\theta_3$) of transition dipoles together with laser driving induces an excitonic AB phase $\Phi$. The anthracene monomers are equidistant $a$ from their neighbors forming a square. (b) Schematic illustration of the mechanism whereby Floquet engineering induces excitonic AB phases. The elliptically polarized field $E_{LD}(t)$ drives the $|E_1\rangle \rightarrow |F_1\rangle$ low-frequency vibrational transition (vertical yellow arrows). Horizontal yellow arrows denote excitonic couplings mediated by electrostatic interactions. In (b1), excitation of the first chromophore at $|E_1\rangle$ is resonantly transferred to the second chromophore $|E_2\rangle$ via a dipolar coupling. Next, the laser promotes the $|E_2\rangle \rightarrow |F_2\rangle$ vibrational excitation, “dialing” phase $\phi_2$ onto that transition. Subsequent excitation transfer $|F_2\rangle \rightarrow |F_3\rangle \rightarrow |F_4\rangle$ occurs via resonant dipolar couplings, after which the laser promotes the $|F_4\rangle \rightarrow |E_4\rangle$ vibrational emission, dialing phase $-\phi_4$ onto that transition. Finally another step of resonant dipole-mediated excitation transfer $|E_4\rangle \rightarrow |E_1\rangle$ closes the loop, yielding an AB phase $\Phi = \phi_2 - \phi_4$. If $\Phi \neq n\pi$ for integer $n$ this signals that time-reversal symmetry broken. Meanwhile (b2) illustrates a pathways that does not result in nontrivial AB phases.
factor that characterizes the displacement of the $S_1$ potential energy surface with respect to the $S_0$ surface is $D = 0.31^{22}$. These parameters were used in previous theoretical studies addressing how to control excitation-energy transfer by manipulating ultrafast vibrational dynamics in anthracene dimers$^{23,24}$; these parameters were fit to experimental data involving vibrational coherences in anthracene dimers$^{25}$. The weak vibronic coupling featured by this transition allows us to simplify the anthracene spectrum as an effective three-level system featuring ground $|g, 0\rangle$ and excited $|e, 0'\rangle$ electronic states with no phonons, and an excited $|e, 1'\rangle$ electronic state with one phonon, where $|g\rangle$ and $|e\rangle$ denote $S_0$ and $S_1$ electronic states, and $|\nu\rangle$ and $|\nu'\rangle$ label vibrational eigenstates of the harmonic potentials corresponding to $S_0$ and $S_1$, respectively (see Figure 1a-c).

For simplicity, let us consider a homotetramer where the chromophores are located at the vertices of a square of side length $a = 3.5$ Å$^{25}$, mimicking values reported in the experimental literature (see 2). As we shall explain below, other more elaborate cyclic aggregates with additional complexities in their spectra can also serve the purposes of our study. To unclutter notation, we will work in the following single-excitation basis:

$$|G\rangle = \prod_{i=1}^{4} |g_i, 0_i\rangle,$$

$$|E_j\rangle = |e_j, 0'_j\rangle \prod_{i\neq j}^{4} |g_i, 0_i\rangle,$$

$$|F_i\rangle = |e_j, 1'_j\rangle \prod_{i\neq j}^{4} |g_i, 0_i\rangle.$$

The excitonic Hamiltonian of the homotetramer reads ($\hbar = 1$),
\[ H_T = \sum_{i=1}^{4} \left( \omega_E |E_i\rangle \langle E_i| + \omega_F |F_i\rangle \langle F_i| \right) \]

\[ + \sum_{\langle ij \rangle} \left[ (J_{E_i,E_j}|E_i\rangle \langle E_j| + J_{E_i,F_j}|E_i\rangle \langle F_j| + J_{F_i,F_j}|F_i\rangle \langle F_j|) + \text{h.c.} \right], \]

(2)

where the sum over \( \langle ij \rangle \) assumes only nearest-neighbor couplings. Here \( \omega_E = \omega_e \) and \( \omega_F = \omega_e + \omega_{\text{vib}} = 28,080 \text{cm}^{-1} \), and \( J_{\alpha\beta} = J_{\beta\alpha} \) are the electrostatic couplings between excitonic states \( |\alpha\rangle \) and \( |\beta\rangle \), which are calculated assuming the Condon approximation \(^{26,27}\), e.g.

\[ J_{E_i,F_j} = \langle e_i g_j | H_T | g_i e_j \rangle \langle 0'_i | 0_i \rangle \langle 0_j | 1'_j \rangle, \]

where

\[ \langle e_i g_j | H_T | g_i e_j \rangle = \eta \frac{(\mu_i \cdot \mu_j) - 3(\mu_i \cdot \hat{r}_{ij})(\mu_j \cdot \hat{r}_{ij})}{a^3} \]

is approximated as the classical dipole-dipole interaction, with \( \mu_i = \langle E_i | \mu | G \rangle = \langle e_i | \mu | g_i \rangle \) being the transition dipole moment vector for the \( S_0 \rightarrow S_1 \) transition for the \( i \)-th chromophore \( (\mu \) is the dipole operator) and \( \hat{r}_{ij} \) being the unit vector that connects chromophores \( i \) and \( j \). The value \( \eta = 1,100 \text{ cm}^{-1} \text{Debye}^{-2} \text{Å}^3 \) has been chosen to account for index of refraction effects of the surrounding medium, so that the dipolar coupling between parallel anthracene molecules is \( \langle e_i g_j | H_T | g_i e_j \rangle = \eta \frac{\mu_i^2}{a^6} = 22.9 \text{ cm}^{-1} \), a value that is consistent with quantum beats in ultrafast spectroscopy experiments where \( |\mu_i| = 0.90 \text{Debye} \). The scalar \( |\langle n'_i | n_i \rangle|^2 = \exp[-D \frac{Dn}{n_i}] \) is the relevant Franck-Condon factor \(^{28}\). In this work, we fix the orientations of \( \mu_2 \) and \( \mu_4 \) to be along the \( \hat{x} \) and \( \hat{y} \) axes in the molecular aggregate frame, while we vary the orientations of \( \mu_2 \) and \( \mu_4 \) at angles \( \theta_1 \) and \( \theta_3 \) (Figure. \(^2\)a shows \( \theta_1 = 45^0 \) and \( \theta_3 = 315^0 \)). For simplicity, we ignore out-of-plane dipole orientations; this is not a necessary condition and could be easily lifted if chemical synthesis favors other geometries.

Given that \( J_{\alpha\beta} \ll \omega_{\text{vib}} \), the exciton eigenstates of \( H_T \) consist of two bands centered at \( \omega_E \) and \( \omega_F \), respectively, with bandwidths \( \sim 2\text{max}|J_{E_i,E_j}|, \sim 2\text{max}|J_{F_i,F_j}| \). Figure \(^3\) shows the
absorption spectrum of an isotropically averaged collection of homotetramers. Notice that due to different Franck-Condon overlaps, the band at $\omega_F$ is narrower than that at $\omega_E$.

Figure 3: Absorption spectrum of an isotropic solution of excitonic homotetramers. The blue spectrum corresponds to the absorption of an isotropic solution of bare excitonic homotetramers, while the orange line corresponds to the absorption of an isotropic solution of laser-driven homotetramers when the driving laser is circularly polarized ($\Delta \phi = \frac{\pi}{2}$). Both are normalized to the maximum absorption of the blue spectrum. Both can be approximately understood as consisting of two bands of transitions: one corresponding to coherent combinations of 0-0’ transitions (centered at $\omega_E$) and 0-1’ transitions (centered at $\omega_F$). The widths of these bands are due to resonant exciton hopping between molecules, and correspond to $\sim 2\text{max}|J_{E_i E_j}|$ and $\sim 2\text{max}|J_{F_i F_j}|$, respectively. (Inset) At a closer look a couple of the peaks are shifted when the system is exposed to a driving laser. This shift is ever so slight due to the fact that the driving laser is weakly coupled to the excitonic tetramers.

Floquet theory for laser-driving

The aforementioned two bands can be mixed upon introduction of a driving laser; the new Hamiltonian is time-dependent and reads,

$$ H_{LD}(t) = H_T - \sum_{i=1}^{4} \mu_{E_i F_i} \cdot E_{LD}(t)|E_i\rangle\langle F_i| + \text{h.c.} \quad (3) $$

where we have invoked an infrared (IR) field at a frequency $\Omega = \omega_{\text{vib}} + \delta$ that is slightly detuned from the $E_i \rightarrow F_i$ vibrational transitions by $\delta$: 

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\[ E_{LD}(t) = \frac{E_{LD}^0}{\sqrt{2}} \cos(\Omega t + \phi_x) \hat{x} + \cos(\Omega t + \phi_y) \hat{y}. \]

The detuning $\delta$ allows us to ignore resonant pumping of vibrational transitions in the ground state (Figure 1b) so that the three-level approximation per molecule (Figure 1c) is justified. The phases $\phi_x$ and $\phi_y$ will play an important role below. The relevant transition dipole moments to the laser-driving are $\mu_{F_iE_i} = \langle F_i | \mu | E_i \rangle = \langle 1'_i | \mu | 0'_i \rangle$ and we take $|\mu_{F_iE_i}| = 0.15$ Debye, which is a reasonable value for IR molecular vibrational excitations.

For completeness, we shall now layout the Floquet theory utilized to address the problem in question. The Hamiltonian $H_{LD}(t)$ is periodic in time with period $T = \frac{2\pi}{\Omega}$ such that $H_{LD}(t + T) = H_{LD}(t)$. The solutions to the time dependent Schrödinger equation (TDSE)

\[ i \frac{d}{dt} |\Psi(t)\rangle = H_{LD}(t) |\Psi(t)\rangle \]

can be written in the Floquet state basis $|\Psi(t)\rangle = \sum_\lambda C_\lambda(t) |\psi_\lambda(t)\rangle$ where

\[ |\psi_\lambda(t)\rangle = e^{-i\varepsilon_\lambda t} |\phi_\lambda(t)\rangle. \quad (4) \]

The Floquet modes can be spectrally decomposed in the single (molecular) excitation basis introduced in Eq. (1),

\[ |\phi_\lambda(t)\rangle = \sum_\alpha |\alpha\rangle \langle \alpha | \phi_\lambda(t) \rangle \]

and are periodic in time with period $T$. Furthermore, they are eigenfunctions of the Floquet Hamiltonian

\[ H_F |\phi_\lambda(t)\rangle = \left[H_{LD}(t) - i \frac{d}{dt}\right] |\phi_\lambda(t)\rangle = \varepsilon_\lambda |\phi_\lambda(t)\rangle, \quad (6) \]

where the eigenvalues $\{\varepsilon_\lambda\}$ are termed quasi-energies. Since $|\phi_\lambda(t)\rangle$ and $H_{LD}(t)$ are time-periodic, we can write Eqs. (5) and (2) in terms of their Fourier components:
\begin{align}
|\phi_\lambda(t)\rangle &= \sum_\alpha \sum_{n=-\infty}^{\infty} |\alpha\rangle \langle \alpha| \phi_\lambda^{(n)} \rangle e^{i n \Omega t}, \\
\langle \alpha| H_{LD}(t) |\beta\rangle &= \sum_{n=-\infty}^{\infty} H_{LD,\alpha\beta}^{(n)} e^{i n \Omega t},
\end{align}

where $H_{LD,\alpha\beta}^{(n)} = \frac{1}{T} \int_0^T dt \langle \alpha| H_{LD}(t) |\beta\rangle e^{-i n \Omega t}$. By substituting Eqs. (7a) and (7b) into Eq. (6), multiplying both sides of the resulting equation by $\exp(-i k \Omega t)$, and taking a time-integral over one period $T$, we obtain

\begin{align}
\sum_{\beta n} H_{F_{\alpha\beta}}^{(k-n)} \langle \beta| \phi_\lambda^{(n)} \rangle &= \varepsilon_\lambda \langle \alpha| \phi_\lambda^{(k)} \rangle, \\
H_{F_{\alpha\beta}}^{(k-n)} &= H_{LD,\alpha\beta}^{(k-n)} + n \Omega \delta_{\alpha\beta} \delta_{kn}.
\end{align}

At this point, we augment the Hilbert space from $|\alpha\rangle$ to $|\alpha\rangle \otimes |t\rangle$, where $\langle t| \phi_\lambda \rangle = |\phi_\lambda(t)\rangle$, and introduce the Fourier basis $\{|n\rangle\}$ where $\langle n| \phi_\lambda \rangle \equiv |\phi_\lambda^{(n)}\rangle$, $\langle t| n \rangle = e^{i n \Omega t}$, $|\alpha, n\rangle \equiv |\alpha\rangle |n\rangle$, and $\langle \alpha, k| H_F|\beta, n\rangle \equiv H_{F_{\alpha\beta}}^{(k-n)}$, transforming the eigenvalue problem into the following:

\begin{align}
H_F|\phi_\lambda\rangle &= \left[H_F^{(0)} + H_F^{(1)}\right]|\phi_\lambda\rangle = \varepsilon_\lambda |\phi_\lambda\rangle, \\
H_F^{(0)} &= \sum_{n=-\infty}^{\infty} \left\{ \sum_{i=1}^{4} \left( (\omega_E + n \Omega)|E_i, n\rangle \langle E_i, n| + (\omega_F + k \Omega)|F_i, n\rangle \langle F_i, n| \right) + n \Omega |Gn\rangle \langle Gn| \\
&\quad + \sum_{(ij)} \left[ (J_{E_i,E_j} |E_i, n\rangle \langle E_j, n| + J_{E_i,F_j} |E_i, n\rangle \langle F_j, n| + J_{F_i,E_j} |F_i, n\rangle \langle E_j, n| + h.c. \right) \right\}, \\
H_F^{(1)} &= -\frac{E_{LD}^0}{\sqrt{2}} \sum_{n=-\infty}^{\infty} \left\{ \sum_{i=1}^{4} \sum_{q=x,y} \left[ \mu_{E_i,F_j}^q e^{i \phi_q} |E_i,n+1\rangle \langle F_i,n+1| + e^{-i \phi_q} |E_i,n+1\rangle \langle F_i,n| + h.c. \right] \right\},
\end{align}
An intuitive interpretation of this basis, which was originally presented by Shirley, comes from associating \( n \) to the number of quanta present in the laser-driving mode; e.g., \(|E_13\rangle\) would refer to the state were the exciton corresponds to the 0-0’ transition in first chromophore while the field contains three photons. Following this interpretation, Eq. (9) denotes the interaction between excitonic states that preserve photon number, while Eq. (9c) shows that the driving field couples states \(|E_i⟩, |F_i⟩\) by either absorbing or emitting a photon. To gain further insights, we consider the limit where

\[
|J_{E_iF_j}|, |\mathbf{\mu}_{LD} \cdot \mathbf{E}_{LD}(t)| \ll \Omega,
\]

so that we can apply the rotating-wave approximation (RWA) to drop highly off-resonant terms; Eqs. (9b) and (9c) can then be reduced to

\[
H^{(0)}_{F(RWA)} \approx \sum_{n=-\infty}^{\infty} \sum_{i=1}^{4} \left( (\omega_E + n\Omega)|E_i n⟩⟨E_i n| + (\omega_F + n\Omega)|F_i n⟩⟨F_i n| \right) + k\Omega|Gn⟩⟨Gn| + \text{h.c.}
\]

\[
H^{(1)}_{F(RWA)} \approx -\frac{E_{LD}^0}{\sqrt{2}} \sum_{n=-\infty}^{\infty} \sum_{i=1,q}^{4} \left( \mu_{E_i F_j}^q (e^{-i\phi_q}|E_i n + 1⟩⟨F_i n| + \text{h.c.} \right)
\]

The RWA invokes a physically intuitive constraint: the laser-driving intensity is weak enough that it can only induce the \(|E_i⟩ \rightarrow |F_i⟩\) transition if the exciton absorbs a photon from the field. Furthermore, the RWA block-diagonalizes Eq. (9a) so that \( H_F \approx \sum_n h_{F,n} \) where the
$n$-th block $h_{F,n}$ is defined as:

$$h_{F,n} = \sum_{i=1}^{4} \left( (\omega_E + (n + 1)\Omega)|E_{i}n + 1\rangle\langle E_{i}n + 1| + (\omega_F + n\Omega)|F_{i}n\rangle\langle F_{i}n| \right) + n\Omega|G_{n}\rangle\langle G_{n}|$$

$$+ \sum_{(ij)} \left( J_{E_{i}E_{j}}|E_{i}n + 1\rangle\langle E_{j}n + 1| + J_{F_{i}F_{j}}|F_{i}n\rangle\langle F_{j}n| \right) + \text{h.c.}$$

$$- \frac{E_{LD}^0}{\sqrt{2}} \sum_{i=1, q}^{4} \mu_{E_{i}F_{i}}^q \left( e^{-i\phi_q}|E_{i}n + 1\rangle\langle F_{i}n| + \text{h.c.} \right).$$

(12)

Note that the Floquet states $\{|\psi_{\lambda}(t)\rangle\}$ are uniquely characterized by the quasi-energies $\varepsilon_{\lambda} \mod \Omega^{13,14}$; therefore, in the RWA, we only need to diagonalize one block $h_{F,n}$ to construct the Floquet state basis $\{|\psi_{\lambda}(t)\rangle\}$. One should note that Eq. (12) resembles a lattice Hamiltonian where the quantum degrees of freedom are influenced by a gauge field $\vec{A}(r)^{29}$, where $\phi_q = \int \vec{A}(r) \cdot dr$. Typically, the latter arises from a magnetic field resulting in AB phases; in our case, we shall see that the gauge field is a result of the elliptically polarized laser driving.

### Calculation of circular dichroism spectrum

To calculate the CD of the laser-driven system, we invoke the formalism developed in $^{15}$.

We compute the rates of absorption $W_{\pm}$ due to weak-intensity continuous-wave circularly-polarized probe laser fields at UV-visible frequency $\omega$

$$E_{P\pm}(\omega, t) = \frac{E_{P}^{0}}{\sqrt{2}} (\cos \omega t \hat{x} \mp \sin \omega t \hat{y}).$$

The CD response at each frequency $\omega$ is defined as the difference $\delta W = W_{+} - W_{-}$ in the rates due to RCP and LCP light,

$$\delta W(\omega) = -|E_{P}^{0}|^2 \pi \text{Im} \left[ \sum_{\lambda, \alpha, \beta} \sum_{n=-\infty}^{\infty} \mu_{\lambda}^\alpha \langle \phi_{\lambda}|\alpha n\rangle \mu_{\beta}^\beta \langle \beta n|\phi_{\lambda}\rangle \delta(\varepsilon_{\lambda} - n\Omega - \omega) \right].$$

(13)

Here $\varepsilon_{\lambda} - \Omega$ denotes the $|G\lambda\rangle \rightarrow |\phi_{\lambda}\rangle$ transition energy, were $|\phi_{\lambda}\rangle$ is an eigenstate of $h_{F,1}$ (see Eq. (12)), $(1 - n)\Omega$ is the energy corresponding to the excitonic system emitting $n - 1$ photons, and $\omega$ is the energy absorbed from the probe. Note that due to the RWA, $h_{F,1}$
only couples states with the same number of photons or those that differ by one photon, so \( n = 1, 2 \), which results in Eq. (13) being simplified to:

\[
\delta W(\omega) = -|E_p^0|^2 \pi \text{Im} \left[ \sum_{\lambda} \sum_{ij} \left\{ \mu_{E_iG}^y \langle \phi_\lambda | E_i 2 \rangle \mu_{G E_j}^x \langle E_j 2 | \phi_\lambda \rangle \delta (\varepsilon_\lambda - 2\Omega - \omega) \\
+ \mu_{F_iG}^y \langle \phi_\lambda | F_i 1 \rangle \mu_{G F_j}^x \langle F_j 1 | \phi_\lambda \rangle \delta (\varepsilon_\lambda - \Omega - \omega) \right\} \right].
\]

Eq. (14) corresponds to the CD for a single homotetramer at a fix orientation. Since we are interested in an isotropic film or solution of such aggregates, we must take an average of \( \delta W \) over different orientations of the tetramer with respect to the incident light \( k \) vector,

\[
\langle \delta W(\omega) \rangle = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \int_0^\pi d\chi d\psi d\theta \sin \theta W(\omega; \chi, \theta, \psi).
\]

where we have explicitly written \( \delta W(\omega) = \delta W(\omega; \chi, \theta, \psi) \) to express the fact that the CD for each aggregate is a function of its orientation, defined by Trait Brian angles angles \( \chi, \theta, \psi \); see Figure 4. Notice that unlike with with perturbative spectroscopy\(^{31}\), we cannot analytically carry out this average given that \( h_{F,1} \) is a function itself of \( (\chi, \theta, \psi) \), as each orientation experiences a different driving due to its different dipole projections with the IR laser. Hence, we compute the isotropically averaged CD spectrum in Eq. (15) via Monte Carlo integration, making sure numerical convergence is achieved by setting a tolerance value (see SI).

**Results and Discussion**

**Excitonic AB phases**

To illustrate the nontrivial effects produced by laser dressing, we now consider coherent pathways due to the various terms in Eq. (12). In particular, we are interested in cyclic pathways, that is, those which begin and end in the same state. For concreteness, let us focus on the pathway depicted in Figure 2b1. Excitation of the first chromophore at \( |E_1\rangle \)
is resonantly transferred to the second chromophore $|E_2\rangle$ via dipolar coupling. Next, the elliptically polarized promotes the $|E_2\rangle \rightarrow |F_2\rangle$ vibrational excitation, imprinting a nontrivial phase $\phi_2$ onto that transition. Subsequent excitation transfer via dipolar coupling $|F_2\rangle \rightarrow |F_3\rangle \rightarrow |F_4\rangle$ is followed by a laser-induced vibrational de-excitation $|F_4\rangle \rightarrow |E_4\rangle$, which imprints yet another nontrivial phase $\phi_4$; the pathway is closed by another dipolar coupling $|E_4\rangle \rightarrow |E_1\rangle$. To make these statements more precise, let us define the Wilson loop corresponding to this pathway,

$$\mathcal{W} = \langle E_1 n | h_{F,n} | E_4 n + 1 \rangle \langle E_4 n + 1 | h_{F,n} | F_4 n \rangle \langle F_4 n | h_{F,n} | F_3 n \rangle$$

$$\times \langle F_3 n | h_{F,n} | F_2 n \rangle \langle F_2 n | h_{F,n} | E_2 n + 1 \rangle \langle E_2 n + 1 | h_{F,n} | E_1 n + 1 \rangle$$

$$= J_{E_1 E_2} \left( \sum_{q=\hat{x},\hat{y}} \frac{E^0_{LD} \mu^q_{E_2 F_2}}{\sqrt{2}} e^{i\phi_q} \right) J_{F_2 F_3}$$

$$\times J_{F_3 F_4} \left( \sum_{q=\hat{x},\hat{y}} \frac{E^0_{LD} \mu^q_{E_2 F_2}}{\sqrt{2}} e^{-i\phi_q} \right) J_{E_4 E_1}. $$

If we define

$$\phi_2 = \arg \left[ J_{E_1 E_2} \left( \sum_{q=\hat{x},\hat{y}} \frac{E^0_{LD} \mu^q_{E_2 F_2}}{\sqrt{2}} e^{i\phi_q} \right) J_{F_2 F_3} \right]$$

$$\phi_4 = -\arg \left[ J_{F_3 F_4} \left( \sum_{q=\hat{x},\hat{y}} \frac{E^0_{LD} \mu^q_{E_2 F_2}}{\sqrt{2}} e^{-i\phi_q} \right) J_{E_4 E_1} \right],$$

the excitonic AB phase corresponding to this pathway is equal to $\Phi = \arg(W) = \phi_2 - \phi_4$. To gain further intuition on the types of transition dipole arrangements that lead to substantial values of $\Phi$, let us consider the configuration in Figure 2a, where the dipoles in chromophores 2 and 4 are aligned along $\hat{x}$ and $\hat{y}$, and the only positive dipolar couplings within our gauge convention is $J_{F_2 F_3}$; then, $\phi_2 = \phi_x$ and $\phi_4 = -\phi_y + 2\pi = -\phi_y$, so that the phases of the
elliptically polarized field are explicitly imprinted in the resulting excitonic AB phase,

$$\Phi = \arg(W) = \phi_x - \phi_y = \Delta \phi.$$ 

A few comments are pertinent at this point. When $\Delta \phi = 0 \text{ mod } \pi$, the driving laser corresponds to linearly polarized light and the AB phase $\Phi = 0, \pi$ is trivial; this is expected as TRS is preserved. However, when $\Delta \phi \neq 0 \text{ mod } \pi$, the driving laser corresponds to elliptically polarized light, leading to a nontrivial AB phase $\Phi \neq 0, \pi$ ($\Delta \phi = \frac{\pi}{2} \text{ mod } \pi$ corresponds to the special case of circular polarization) that signals TRS breaking. Hence, our design crucially depends on chromophores 2 and 4 obtaining different phases $\phi_x$ and $\phi_y$ from the laser-driving; to maximize this difference, they are placed perpendicular to one another. However, the production of a nontrivial AB phase relies also on having coherent dipolar couplings throughout the aggregate that yield a nonzero Wilson loop. To ensure that chromophores 2 and 4 are coupled, chromophores 1 and 3 are positioned along optimal orientations $\hat{x} \pm \hat{y} \sqrt{2}$ so that the exciton hoppings are enough to ensure large coherent couplings throughout the cycle. It follows that to realize an exciton AB phase $\Phi = \frac{\pi}{2}$, one simply needs to set $\Delta \phi = -\frac{3\pi}{2}$, corresponding to right circularly polarized light. At this point, it is worth highlighting that this excitonic AB phase is independent of laser intensity so long as the RWA is a good approximation. This should be contrasted with the analogous electronic AB phase, where giant magnetic fields would be needed to generate a phase $\Phi = \frac{\pi}{2}$ in the nanoscale. In fact, considering a putative loop of the same area $a^2$ as our molecular aggregate, $\Phi = \frac{eBa^2}{\hbar}$ would require $B = 8400$ Tesla (an intensity that is only feasible at present in white dwarfs\textsuperscript{32}. While excitonic and electronic AB phases cannot be compared to one another directly, this remark implies that excitonic AB phases should be substantially easier to realize in nanoscale systems than their electronic counterparts and could open doors to new ways of coherently controlling excitonic processes in molecules and nanomaterials.

Our proposal to induce AB phases via Floquet engineering is heavily influenced by\textsuperscript{12}...
where the authors suggest the periodic modulation of permittivities in arrays of coherently coupled resonators to generate pseudomagnetic fields. Crucial to their setup is a distribution of modulation phases which is locally controlled with electrical circuit elements. This local control of phases is possible in mesoscopic systems but much harder to realize in the nanoscale. In fact, one could be tempted to think that light-matter interaction is ineffective in doing so, given the mismatch between the lengthscale of light and molecules. However, as we show in our example above, we achieve the distribution of modulation phases by exploiting (a) the phase lag between the $\hat{x}$ and $\hat{y}$ components of the electric field of elliptically polarized laser light and (b) by designing rings of coherently coupled molecular dipoles where different sites feature orientations that interact with different polarizations of the laser light.

![Diagram](image)

**Figure 4:** (a) Excitonic homotetramer unit. (b) Depiction of isotropic ensemble of homotetramers; calculation of circular dichroism (CD) involves averaging over orientations $\chi, \theta, \psi$ with respect to the $\mathbf{k}$ vector of the incident beam.

**Features of the CD spectrum**

To test the effects of TRS breaking due to nontrivial excitonic AB phases, Figure 5 shows the isotropic averaged CD spectrum $\langle \delta W(\omega) \rangle$ normalized to the maximum absorption of the isotropic solution in the absence of driving. For our simulations, we use $E_{LD}^0 = 2.7 \times$
$10^7 \frac{V}{m}$, which is a standard value utilized in Floquet engineering experiments with inorganic semiconductors, and take $\delta = -0.1 \omega_{vib}$. With these parameters we obtain $|\mu_{LD} \cdot E_{LD}(t)| = 0.002$, which satisfied the requirement of Eq. (10) above. As expected, when $\Delta \phi = 0, \pi$, $\langle \delta W(\omega) \rangle$ vanishes for all $\omega$ as expected: TRS is preserved under linearly polarized light driving. However, arbitrary elliptically polarized fields ($\Delta \phi \neq 0, \pi$) give rise to nonzero CD, where a clear pattern of sign switches occurs at the TRS points. Notice that despite the laser-driving being weak in comparison to its carrier frequency, $|\mu_{LD} \cdot E_{LD}(t)| \ll \Omega$, the small shifts in peak frequencies in Figure 3 give rise to substantial CD signals, just like in MCD, where moderate values of magnetic fields can easily dissect congested spectra. Regardless, we notice a clear progression of the spectrum as a function of $\Delta \phi$, although these energy changes are very small with respect to $\omega_{vib}$, as a consequence of Eq. (10). Also note that the maximum absolute value of $\langle \delta W(\omega) \rangle$ occurs at $\Delta \phi = \frac{\pi}{2}, \frac{3\pi}{2}$, which corresponds to circularly polarized light. Based on the mechanism outlined in the previous subsection (see also Figures 2a, b), we attribute this symmetry to the fact that in our homotetramer, the dipoles are all the same magnitude.

Figure 5: Computed circular dichroism (CD) spectrum for isotropic ensemble of molecular homotetramers under the influence of elliptically-polarized driving. Here $\langle \delta W(\omega) \rangle$ is normalized with respect to the maximum absorption of the isotropic system when there is no laser driving. Clear progressions of the CD as a function of ellipticity $\Delta \phi$ can be observed, with sign switches at the time-reversal-symmetry (TRS) points $\Delta \phi = 0, \pi$. 

Figure 5: Computed circular dichroism (CD) spectrum for isotropic ensemble of molecular homotetramers under the influence of elliptically-polarized driving. Here $\langle \delta W(\omega) \rangle$ is normalized with respect to the maximum absorption of the isotropic system when there is no laser driving. Clear progressions of the CD as a function of ellipticity $\Delta \phi$ can be observed, with sign switches at the time-reversal-symmetry (TRS) points $\Delta \phi = 0, \pi$. 

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Conclusion

In this article, we have demonstrated that Floquet engineering with elliptically-polarized laser fields can serve as an alternative to magnetic fields to induce pseudo-MO effects in molecular systems and nanomaterials. These phenomena should be regarded as complementary to MCD and MOR effects in molecular systems. Small cyclic molecular aggregates with anisotropic arrangement of transition dipoles can support a wide range of excitonic AB phases upon elliptically polarized laser-driving despite the small areas they enclose. A rich ellipticity-dependent modulation of energy level splittings ensues, which concomitantly manifests in widely tunable CD spectra. Within the program of harnessing coherence in light-harvesting systems\textsuperscript{34}, our study emphasizes the potential that AB phases have in the coherent control of energy and charge transport in molecular aggregates, as well as in the decongestion of spectra of the latter. While we have proposed the realization of excitonic AB phases in topologically protected porphyrin arrays\textsuperscript{17}, such effects have been barely explored in a broader range of systems and they could be appealing as a way to switch exciton couplings and propagation direction on and off on demand rather than by synthetic modification. Moreover, we have recognized that excitonic AB effects are dramatically less challenging to realize than their electronic counterparts. In fact, the nanoscale excitonic AB phases that arise in our designed system depend on the pump laser ellipticity $\Delta \phi$ and not on its field strength; thus a large phase of $\Phi = \pi/2$ can in principle be readily realized in our protocol. This ease must be contrasted with the prohibitive magnetic fields that must be used in nanorings to induce an electronic AB phase of the same magnitude (we must mention, however, ingenious molecular electronics proposals to harness small AB phases arising from weak magnetic fields to induce substantial control on electronic currents\textsuperscript{35}). Finally, it is important to emphasize that while general features of pseudo-MO and MO effects are similar (they both arise from breaking of TRS), they cannot be easily compared\textsuperscript{18}, the former depends on coupling of time-varying electric fields with electric transition dipole moments, while the latter arises from the interaction of static magnetic fields with the spin and orbital angular...
momentum of molecular eigenstates. Yet, we suspect that pseudo-MO effects could provide a convenient alternative in situations where magnetic fields are experimentally unfeasible.

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