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SUPPLEMENTARY MATERIAL TO

Application of Floquet theory and improvement of electron current flow control in a 1D Fe–Cu molecular chain

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VARIATION OF THE HYBRIDIZATION STRENGTH

To discuss in more details the shift, of the resonant peak of 1D Fe-Cu molecular chain, towards a higher frequency, it was prepared a corresponding Matlab code, designed to illustrate the potential shift of the resonant frequency of a 1D Fe-Cu molecular chain towards higher frequencies. A variation of the chosen parameter (V) was considered to enable the discussed shift in the resonant frequency, confirming the effect of hybridization strength on Floquet band structure, Fig. S-1.

As it known, a shift in the resonant frequency can be achieved by modifying the parameters, affecting the energy gap in the investigated hybridized 1D Fe-Cu molecular chain Floquet band structure. Although three parameters affect the energy gap: V, on-site energy, and hopping amplitude,[1] for simplicity, the influence of only one parameter, the hybridization strength, will be commented here.

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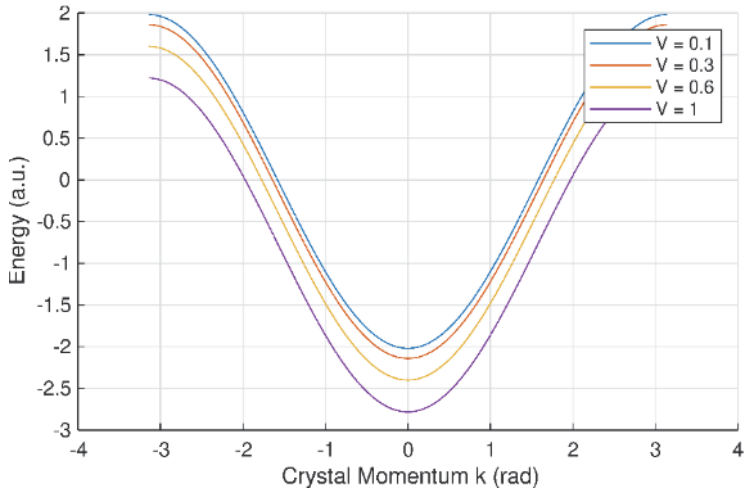

Fig. S-1. Floquet quasi-energy bands of the 1D Fe–Cu molecular chain for different orbital hybridization strengths V. Increasing V (color-coded curves) widens the static energy gap at k=0 and shifts the Floquet resonance to higher photon frequencies. The horizontal axis shows crystal momentum k in units of π/a (with lattice spacing a), and the vertical axis shows quasi-energy in eV. Static orbital hybridization is distinct from Floquet mixing with photon states.

Fig. S-1 represents the effect of increasing the hybridization strength parameter to shift the resonance frequency upward. Let us recall here that the parameter V represents the strength of orbital overlap or hybridization between Fe and Cu orbitals. Increasing the strength of hybridization widens the energy gap between the two hybridized bands, effectively increasing the minimum energy difference at k=0. Since the resonant photon frequency ω roughly corresponds to this energy gap, increasing V shifts the resonance towards a higher ω. In other words, applying external conditions (such as temperature, pressure or strain), that induces a higher amount of orbital overlap or stronger hybridization, can lead to a shift in the resonance photon frequency towards a higher frequency range.

EQUATIONS

Equations employed in the electrochemical study

After postulation of the modeled Hamiltonian, in the second part of the study, further mathematical treatment of the given system, which enabled monitoring of leads and vibrations, considered the postulation of the master equation.[2] The master equation was solved numerically in MATLAB using standard linear algebra routines to propagate the reduced density matrix in time until steady state. This numerical propagation captures the coherent evolution due to the time-dependent Hamiltonian and the incoherent dissipative effects due to coupling with the leads and vibrational baths.

Accordingly, several approximations have been considered, such as: Born approximation (it is supposed weak coupling between molecule and leads, so that the leads remain in equilibrium states),[3] Markov approximation (memory effects are neglected, and it was proposed that the dynamic is dependent only on the current ρ(t)),[4] secular approximation (fast oscillating off-diagonal elements (dependent on energy gaps) are neglected),[5] wide band approximation (the leads density of states assumed to be energy independent, close to the Fermi level),[6] and finally, it is proposed that the leads are in thermal equilibrium (with chemical potentials μ_L, μ_R to model bias). As a result, it was possible to discuss electron tunneling under bias voltage, vibrational coupling, and external driving.

The master equation has the form of the expression, eq. (S1):

$$\frac{d}{dt}\rho(t) = \frac{-i}{\hbar}[H_{mol} + H_{mol-vib} + H_{drive}, \rho(t)] + L_{leads}[\rho(t)] + L_{vib}[\rho(t)] \quad \text{(S1)}$$

where the commutator is used to describe the coherent evolution under the system Hamiltonian, and the external driving; L_{leads} is the dissipative superoperator for electron tunneling, associated with the leads, while L_{vib} is the dissipative superoperator for the vibration environment, reflected in the phonon damping. Eq. (S1) is equivalent to eq. (11), in the main text; it is written here in expanded form to show the contributions from leads and vibrational baths explicitly.

The total Hamiltonian, related to the time-dependent driving term (ultrafast laser), is given by the expression below:

$$H_{drive}(t) = A\cos(\omega t)\hat{O} \quad \text{(S2)}$$

In eq. (S2), the operator magnitude represents the operator coupled to the driving.

Finally, the current from the lead is calculated by applying eq. (S3):

$$I_a(t) = eTr(J_a[\rho(t)]) \quad \text{(S3)}$$

where J_a represents the current superoperator, attributed to electrons tunneling through the lead a, and e is the elementary charge. Given expression corresponds to the actual physical current in amperes.

Numerical treatment of the postulated model enabled the preparation of a Matlab code, the execution of which enabled a visual representation of the modeling of the dependence of the electronic current on the bias, in the case of a 1D Fe-Cu chain. The results are shown in Fig. S-2, representing electron current dependence on the bias, for different driving amplitudes (A) and frequencies (ω).

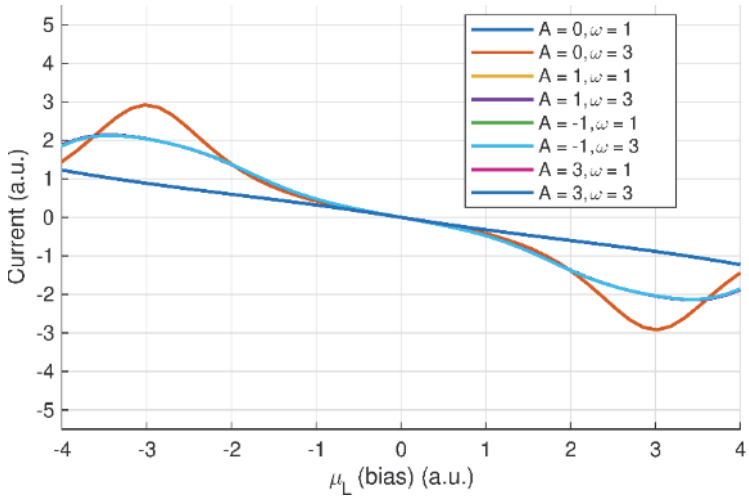

Fig. S-2. Steady-state electron current I (vertical axis, in nA) as a function of applied bias voltage V_{bias} (horizontal axis, in V), for three Floquet driving regimes: absence of driving: A=0, ω=1 eV (blue curve), moderate driving: A=−1, ω=3 eV (light blue curve), and strong driving: A=3, ω=3 eV (dark blue curve). The periodic driving term (Acos(ωt)) modulates the molecular energy levels, influencing electron tunneling probabilities. The curves illustrate photon-assisted current enhancement and suppression effects. All results are obtained using the master equation and parameters in Table I (main text).

Fig. S-2 represents the dependence of electron on bias, for different driving amplitudes (A) and frequencies (ω). Each curve corresponds to different driving amplitudes A and frequencies ω of the periodic driving of the system. Floquet driving, reflected in the term Acos(ωt), affects the curves describing the dependence of the bias on the electric current flowing through the modeled system, modulating the energy levels of the system. As a result, changing quantum states affects the electron tunneling probabilities. Variation in the driving amplitude and frequency impacts the resonance conditions, and consequently, the current.

Only three basic cases were considered, obtained by varying the driving amplitude: absence of driving, moderate driving, and strong driving. In the case when the driving amplitude is zero (absence of driving), the current occurs only due to the static bias. In the case when A = ±2 (moderate driving), the current depends on the phase and frequency, and can consequently be amplified or suppressed. This is more pronounced in the case of A = ±3, where strong driving can cause nonlinear effects, affecting the current in a way that results in suppression or more complex behavior. Accordingly, three selected cases are presented in Fig. 4, illustrating curves representing three basic regimes: the dark blue curve, representing strong driving (A = 3, ω = 3), the light blue curve (moderate driving, A = -1, ω = 3), and the red curve (no driving case, A = 0, ω = 1). The influence of the driving and LMI was explained in terms of the laser

influence, whose interaction with the Fe-Cu molecular chain triggered photo-induced forces. As a final result, change in the tunneling rates occurs. Consequently, fine tuning of the driving amplitude and frequency, enables the enhancement of electron transport via photon-assisted processes.

REFERENCES

1. K. Blum, H. Kleinpoppen, *Phys. Rep.* **52** (1979) 203 (http://doi.org/10.1016/0370-1573(79)90031-0)
2. A. Nordsieck, Jr W. E. Lamb, G. E. Uhlenbeck, *Physica* **7** (1940) 344 (http://doi.org/10.1016/S0031-8914(40)90102-1)
3. M. Born, *Z. Phys* **38** (1926) 803 (http://doi.org/10.3367/UFNr.0122.197708g.0632)
4. S. Nakajima, On quantum theory of transport phenomena: Steady diffusion. *Prog. Theor. Phys* **20** (1958) 948 (http://doi.org/10.1143/PTP.20.948)
5. E. B. Davies, *Commun. Math. Phys.* **39** (1974) 91 (http://doi.org/10.1007/BF01608389)
6. A. P. Jauho, N. S. Wingreen, Y. Meir, *Phys Rev B* **50** (1994) 5528 (http://doi.org/10.1103/PhysRevB.50.5528).