

Supporting Information

The role of magnetic-electric coupling in exciton-coupled ECD spectra. The case of bis-phenanthrenes.

Sandro Jurinovich, Ciro A. Guido, Torsten Bruhn, Gennaro Pescitelli, Benedetta Mennucci

1. Computational Details and additional data

Excited states of phenanthrene monomeric unit

Phenanthrene has been optimized in *vacuum* at B3LYP/6-311G(d) level of theory under C_{2v} symmetry constraint. The excited states were computed by TD-DFT and different functionals were tested. In Table S1 available reference results of phenanthrene transitions are compared with TD-DFT/cc-pVTZ results.

Platt	Symm	CCSDR(3) ^a			CASPT2 ^b		B3LYP		PBE0		PBE0-1/3		CAMB3LYP	
		E (eV)	E (eV)	<i>f</i>	E (eV)	<i>f</i>	E (eV)	<i>f</i>	E (eV)	<i>f</i>	E (eV)	<i>f</i>		
L _b	2A1	4.02	3.42	0.000	3.96	0.001	4.06	0.002	4.17	0.002	4.24	0.001		
L _a	1B2	4.81	4.37	0.038	4.20	0.058	4.30	0.006	4.40	0.006	4.51	0.063		
	2B2	5.02	4.26	0.000	-	-	-	-	-	-	-	-		
B _a	3A1	5.27	4.56	0.268	4.71	0.106	4.84	0.118	5.00	0.137	5.23	0.175		
B _b	3B2	5.44	4.81	1.218	4.95	0.648	5.06	0.723	5.19	0.810	5.29	0.730		
B _a vs B _b		0.17	0.25	(0.220)	0.24	(0.163)	0.22	(0.163)	0.18	(0.169)	0.06	(0.239)		

Table S1. Excitation energies and oscillator strengths (*f*) for the first excited states of phenanthrene. [a] From ref.1. [b] From ref. 2. Last row: energy difference (eV) between B_a and B_b transitions and oscillator strength ratio B_a/B_b in parenthesis.

In this study we are interested in the B transitions (in Platt's nomenclature³) that are responsible of the strong exciton couplet in the CD spectra. The energy difference between B_b and B_a is sensitive to the functional and ranges from 0.06 eV for CAMB3LYP to 0.24 eV for B3LYP. Post Hartree-Fock calculations have determined an energy difference in the range 0.17 – 0.25 eV with an oscillator strength ratio of 0.22 in the case of CASPT2. The functional PBE0-1/3 is in good agreement with CCSDR(3) calculations for that concerns the B_b - B_a energy difference and also gives a reasonable ratio between B_a/B_b oscillator strengths if compared with CASPT2 results. The basis set cc-pVTZ

was chosen in order to obtain a good agreement between transition dipole moments calculated in both length and velocity gauge formulations (see section 2).

Excitonic calculation

Bis-phenanthrene model systems were built by connecting the two optimized monomeric units in 1-1' and 4-4' ring positions. The length of the bond connecting the two monomers was optimized keeping all the other internal coordinates frozen. The geometrical parameters used are reported below.

	r (Å)	Dihedral (τ)	τ (deg)
1,1'-bPh	1.506	10-1-1'-10'	90
4,4'-bPh	1.501	3-4-4'-3'	90

Table S2. B3LYP/6-311G(d) geometrical parameters of Bis-phenanthrene model systems

For both systems the computed PBE0-1/3/cc-pVTZ excited states were compared to the results with the excitonic calculations performed at the same level. We also performed excitonic calculations at different monomer distances, ranging from 1.5 Å to 8.0 Å, and compared the difference between the complete ($\mu\text{-}\mu\text{+}\mu\text{-m}$) and approximated ($\mu\text{-}\mu$) formulations. Here, the spectra corresponding to Figure 2 of the paper are reported in Figure S1 and S2.

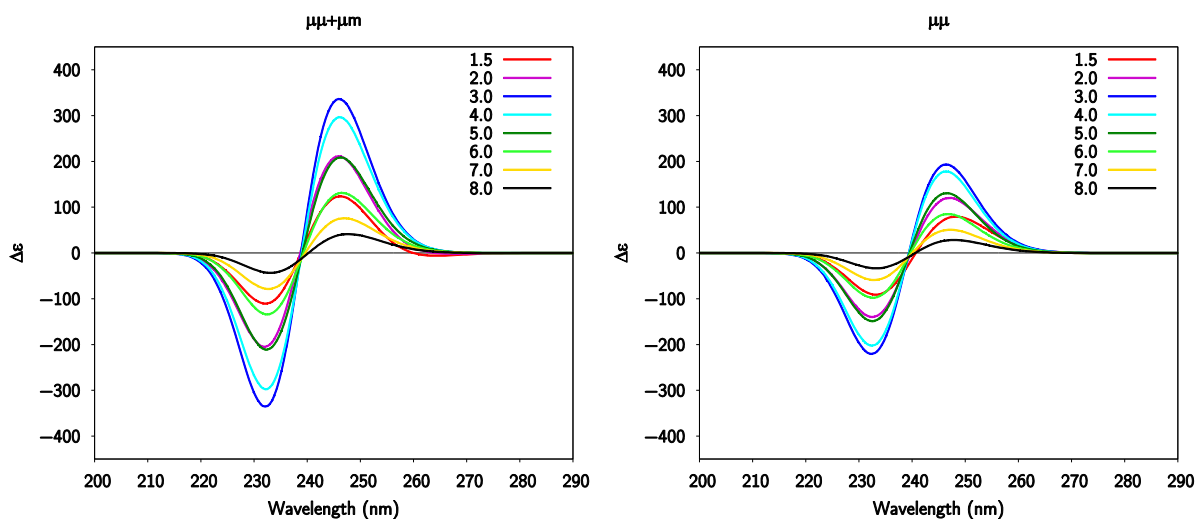


Figure S1. EC-CD spectra of 4,4'-bis-phenanthrene at different 4-4' distances using the complete (left) and approximated (right) formulations for the couplings of rotatory strength equation at PBE0-1/3/cc-pVTZ level of theory. The bandwidth of spectra is 0.15 eV.

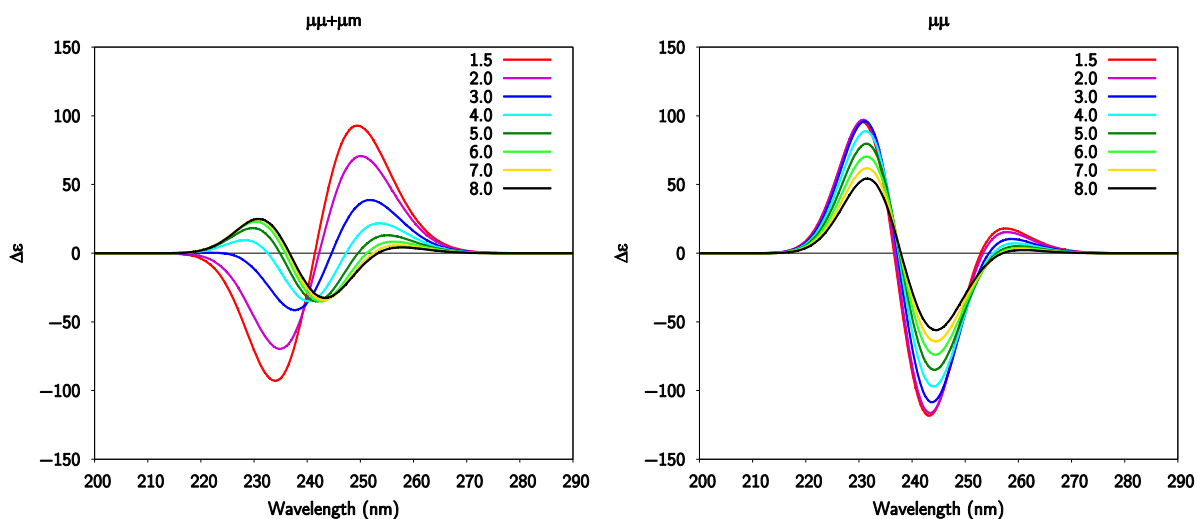


Figure S2. EC-CD spectra of 1-1'-bis-phenanthrene at different 1-1' distances using the complete (left) and approximated (left) formulations for the couplings of rotatory strength equation at PBE0-1/3/cc-pVTZ level of theory. The bandwidth of spectra is 0.15 eV.

The sign inversion of the couplet can be also qualitatively estimated by comparing the excitonic rotational strengths for 1B_a and 1B_b couplets of the two model systems, shown in Figure S3. For the most intense 1B_b transition, only the complete formulation shows a clear sign inversion in the case of 1,1'-bis(phenanthrene) system increasing the chromophoric distance.

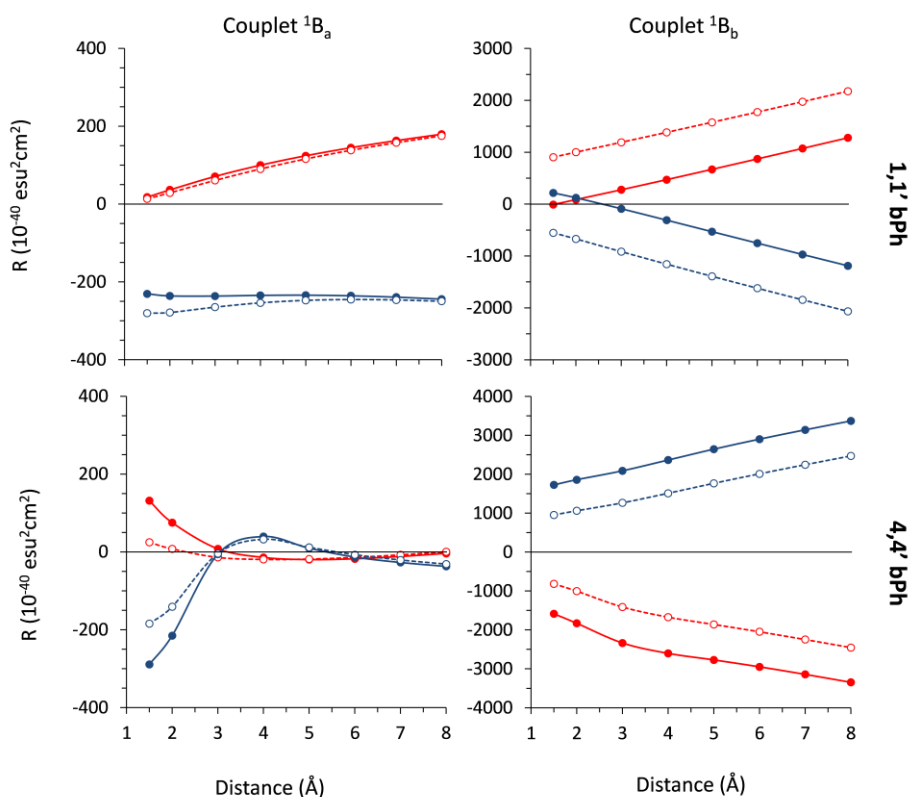


Figure S3. Excitonic rotational strengths for 1B_a and 1B_b couplets of the two model systems. Solid lines corresponds to the total rotational strengths whereas the dashed lines are referred to the approximated $\mu\text{-}\mu$ term only. The distance is referred to 1-1' and 4-4' carbons.

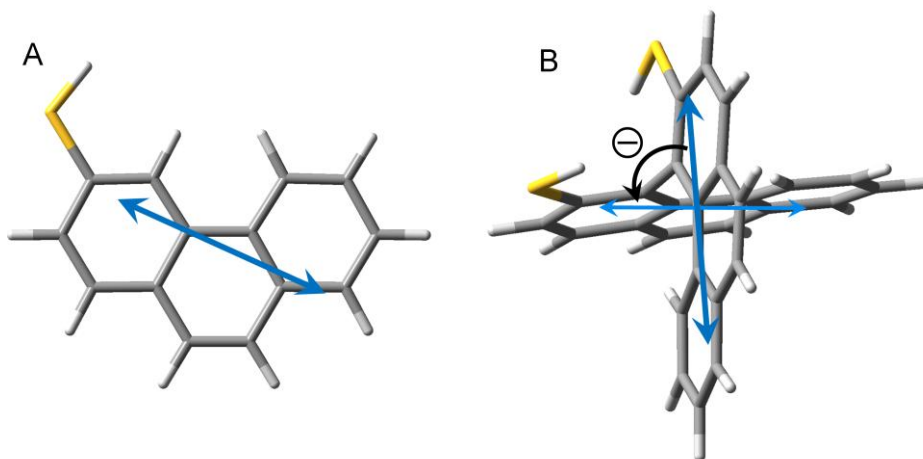


Figure S4. A. Orientation of 1B_b transition dipole moment in phenanthrene-3-thiol, from PBE0-1/3/cc-pVTZ calculations. B. Exciton chirality rule for the coupling of 1B_b ETDMs in compound (aR)-1a.

2. The gauge-independent QM Excitonic CD scheme in EXAT.

In the EXAT⁴, we implemented and tested a gauge-independent QM based computational protocol for CD spectra simulation in an excitonic scheme.

The goal is to compute the rotational strength R for a transition from the ground ($|0\rangle$) to a generic excited state ($|K\rangle$), determined by the Rosenfeld equation:

$$R_{0K} = \text{Im}(\langle 0|\boldsymbol{\mu}|K\rangle \cdot \langle K|\mathbf{m}|0\rangle) \quad (1)$$

In order to extend this approach to a multichromophoric system, one needs to compute the transition properties by an excitonic model. The macromolecule is divided into groups that are independent (i.e. they are assumed to not exchange electrons) but coupled through Coulombic, exchange-correlation and overlap interactions.

The Hamiltonian of the total system can be therefore expressed as:

$$\hat{H} = \sum_i^N \hat{H}_i + \sum_{i,j} \hat{V}_{ij} \quad (2)$$

where \hat{H}_i is the Hamiltonian for the unit i , and \hat{V}_{ij} is the coupling between two different units i and j . These couplings are determined by the transition densities associated to the different excitations on the chromophoric units. For instance, the Coulombic terms are expressed as:

$$\hat{V}_{ij}^{Coul} = \int d\mathbf{r}d\mathbf{r}' \tilde{\rho}_i^*(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \tilde{\rho}_j(\mathbf{r}') \quad (3)$$

The excitonic ground state ($|0\rangle$) can be written as a product of the localized unperturbed ground states of the single chromophores (Φ_0^i) whereas the excitonic wavefunctions ($|K\rangle$) can be written considering a linear combination of wavefunctions of single excited states (Ψ_a^i) expressed as singly excited state of each chromophoric units (Φ_a^i) at time. The expansion coefficients (C_{i0a}^K) are obtained diagonalizing the Hamiltonian matrix (eq. 7).

$$|0\rangle = \prod_i \Phi_0^i \quad (4)$$

$$\Psi_a^i = \Phi_a^i \prod_{j \neq i} \Phi_0^j \quad (5)$$

$$|K\rangle = \sum_{i,a} C_{i0a}^K \Psi_a^i = \sum_{i,a} C_{i0a}^K \Phi_a^i \prod_{j \neq i} \Phi_0^j \quad (6)$$

Therefore, the excitonic properties can be obtained as the linear combination of the corresponding ones relative to a transition $0 \leftarrow a$ on the chromophore i , obtained by QM calculations:

$$\begin{aligned} \langle 0 | \boldsymbol{\mu} | K \rangle &= \left\langle \prod_i \Phi_0^i \left| \boldsymbol{\mu} \right| \sum_{i,a} C_{i0a}^K \Phi_a^i \prod_{j \neq i} \Phi_0^j \right\rangle = \\ &= \sum_{i,a} C_{i0a}^K \langle \Phi_0^i | \boldsymbol{\mu} | \Phi_a^i \rangle = \sum_{i,a} C_{i0a}^K \boldsymbol{\mu}_{i0a} \end{aligned} \quad (7)$$

$$\begin{aligned} \langle 0 | \mathbf{m} | K \rangle &= \mathbf{m}_{0K} = \left\langle \prod_i \Phi_0^i \left| \mathbf{m} \right| \sum_{i,a} C_{i0a}^K \Phi_a^i \prod_{j \neq i} \Phi_0^j \right\rangle = \sum_{i,a} C_{i0a}^K \langle \Phi_0^i | \mathbf{m} | \Phi_a^i \rangle = \\ &= \sum_{i,a} C_{i0a}^K \mathbf{m}_{i0a} \end{aligned} \quad (8)$$

$$R_{0K} = \text{Im} \left\{ \sum_{i,j}^n \sum_{a,b}^m C_{i0a}^K C_{j0b}^K [\boldsymbol{\mu}_{i0a} \cdot \mathbf{m}_{j0b}] \right\} \quad (9)$$

The definition of the Rosenfeld relation, as expressed in eq. 1 or eq. 9, is however gauge-dependent, as a consequence of the first König theorem applied to the total magnetic moment \mathbf{m} :

$$\begin{aligned} \langle K | \mathbf{m} | 0 \rangle &= \langle K | \mathbf{m}^{int} | 0 \rangle - i \frac{e\hbar}{2m_e c} \mathbf{R}_{CM} \times \langle K | \nabla_{CM} | 0 \rangle = \\ &= \sum_{i,a} C_{i0a}^K (\mathbf{m}_{i0a}^{int} - \mathbf{R}_i \times i \frac{e\hbar}{2m_e c} \nabla_{i0a}) \end{aligned} \quad (10)$$

In eq. 10, \mathbf{m}^{int} is the intrinsic magnetic moment and \mathbf{R}_{CM} is the vector of center of mass. A gauge-independent expression can be obtained in two different ways by the use of the commutator $[\hat{H}, \mathbf{r}]$:

$$[\hat{H}, \mathbf{r}] = \frac{e\hbar^2}{m_e} \nabla \quad (11)$$

In the dipole-length gauge, eq. 11 is applied to the extrinsic component of the magnetic moment:

$$\langle 0|\nabla|K\rangle = \frac{m_e(\mathcal{E}_0 - \mathcal{E}_K)}{e\hbar^2} \langle 0|\boldsymbol{\mu}|K\rangle = -\frac{2\pi m_e v_{K0}}{e\hbar} \langle 0|\boldsymbol{\mu}|K\rangle \quad (12)$$

After some algebra, the equation 9 therefore can be rewritten as:

$$R_{0K} = \text{Im} \left\{ \sum_{i,j}^n \sum_{a,b}^m C_{i0a}^K C_{j0b}^K \left[\boldsymbol{\mu}_{i0a} \cdot \mathbf{m}_{j0b}^{int} + i \frac{v_{j0b}}{c} (\boldsymbol{\mu}_{i0a} \cdot \mathbf{R}_{ij} \times \boldsymbol{\mu}_{j0b}) \right] \right\} \quad (13)$$

This equation corresponds to the equation reported in the paper.

In the dipole-velocity gauge, vice versa, the electric dipole moment is expressed in function of the ∇ operator by mean of the commutator $[\hat{H}, \mathbf{r}]$:

$$\begin{aligned} \langle 0|\boldsymbol{\mu}|K\rangle &= \frac{e\hbar^2}{m_e(\mathcal{E}_0 - \mathcal{E}_K)} \langle 0|\nabla|K\rangle = -\frac{e\hbar}{2\pi m_e v_{K0}} \langle 0|\nabla|K\rangle = \\ &= -\frac{e\hbar}{2\pi m_e v_{K0}} \left\langle \prod_i \Phi_0^i \left| \nabla \right| \sum_{i,a} C_{i0a}^K \Phi_a^i \prod_{j \neq i} \Phi_0^j \right\rangle = \\ &= -\frac{e\hbar}{2\pi m_e v_{K0}} \sum_{i,a} C_{i0a}^K \langle \Phi_0^i | \nabla | \Phi_a^i \rangle = -\frac{e\hbar}{2\pi m_e v_{K0}} \sum_{i,a} C_{i0a}^K \nabla_{i0a} \quad (14) \end{aligned}$$

After some algebra, the equation 9 therefore can be rewritten as:

$$R_{0K} = -\frac{e\hbar}{2\pi m_e} \text{Im} \left\{ \frac{\sum_{i,j}^n \sum_{a,b}^m C_{i0a}^K C_{j0b}^K [\nabla_{i0a} \cdot \mathbf{m}_{j0b}]}{v_{K0}} \right\} \quad (15)$$

The final algorithm involves the following steps:

1. Compute the transitions of interest for each isolated chromophoric unit.
2. Compute the couplings between all the chromophoric pairs (eq. 3).
3. Build the excitonic Hamiltonian and diagonalize it (eq. 2).
4. Compute the excitonic transition dipoles (eqs. 7-8)
5. Compute the rotational strength in dipole (eq. 9) or velocity (eq. 15) gauge formulation.

As a final comment, it is worth to note that the use of the commutator in equation 11 is valid for exact wavefunctions or in a large basis set limit. Therefore, in order to be consistent, for a given basis set the transition dipole moments of single chromophores in both length and velocity gauge should differ less than 0.1 a.u.

References

- [1] H. H. Falden, K. R. Falster-Hansen, K. L. Bak, S. Rettrup, S. P. A. Sauer, *J. Phys. Chem. A* **2009**, 113, 11995-12012.
- [2] R. González-Luque, L. Serrano-Andrés, M. Merchán, M. P. Fülcher, *Theor. Chem. Acc.* **2003**, 110, 224-232.
- [3] J. R. Platt, *J. Chem. Phys.* **1949**,17, 484-495.
- [4] S. Jurinovich, C. A. Guido, B. Mennucci, EXAT (Excitonic Analysis Tool), University of Pisa, Italy, 2014, <https://www1.dcci.unipi.it/molecolab/tools/> .