Importance of the Vibronic Effects In Chiroptical Spectra

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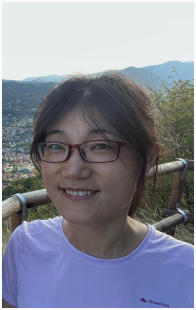
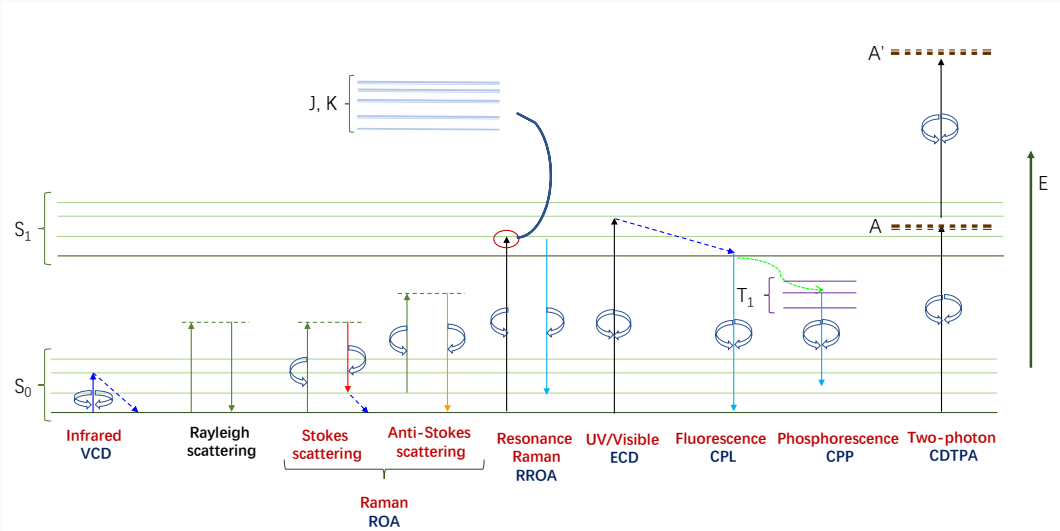
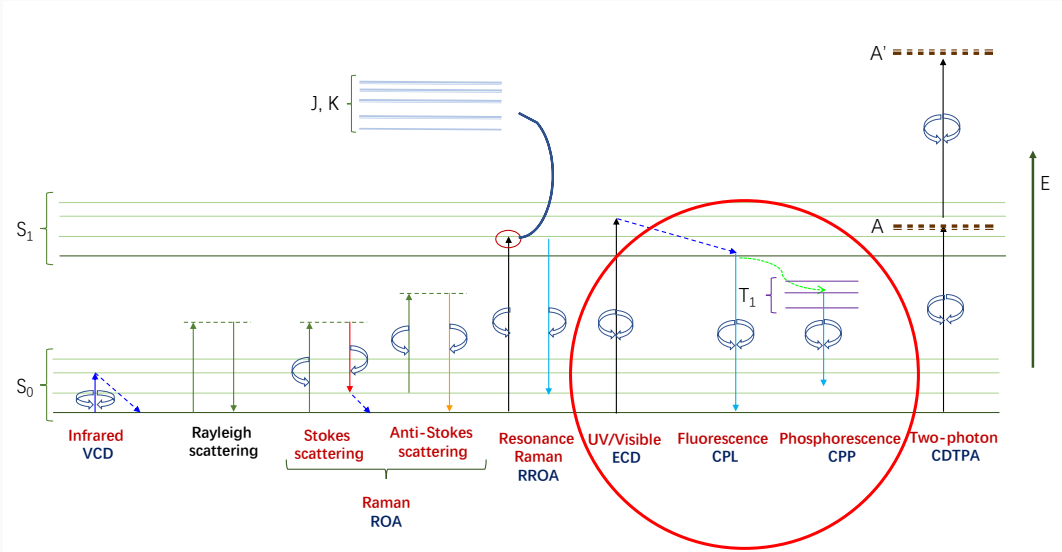


Photon processes

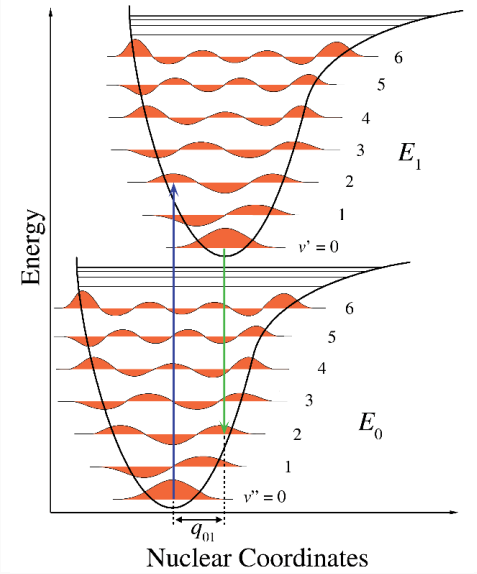


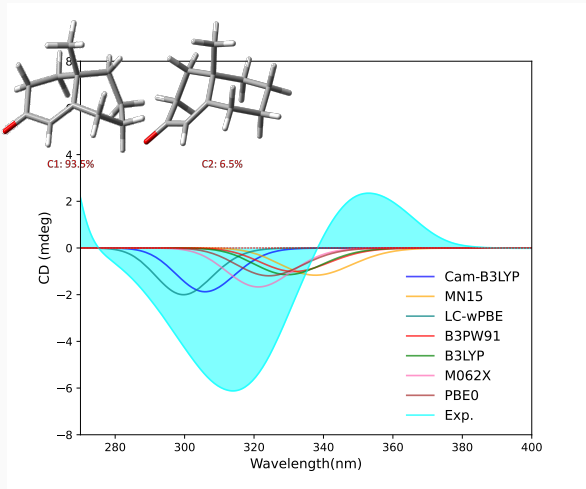
Photon processes



UV-vis (electronic) spectra

Vibronic simulations



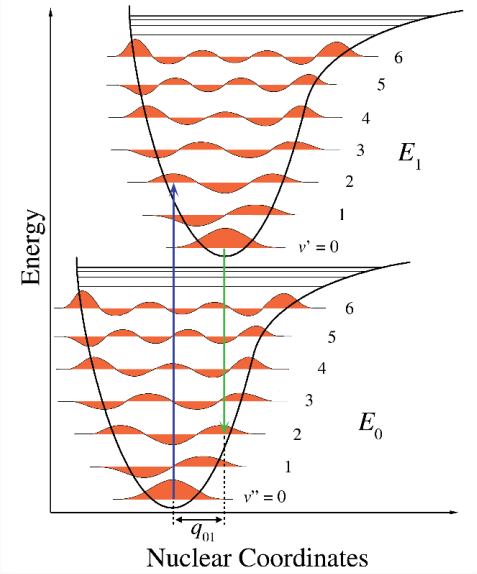


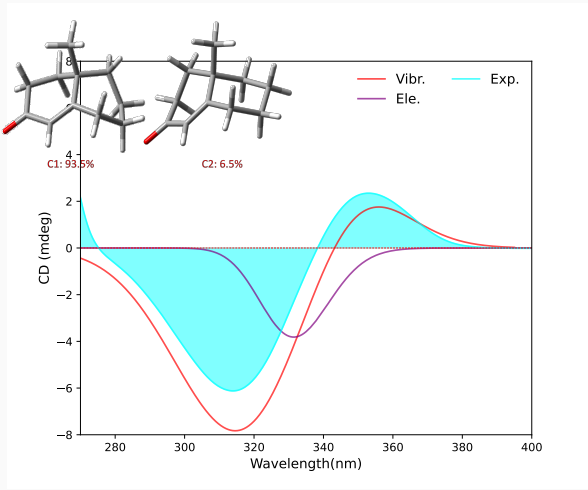
ECD spectrum of naphthaletone

No ESCM can predict positive band

J. Bloino, A. Baiardi, M. Biczysko, *International Journal of Quantum Chemistry* **116**, 1543–1574 (2016), A. Baiardi, J. Bloino, V. Barone, *The Journal of Chemical Physics* **144**, 084114 (2016).

Vibronic simulations





ECD spectrum of naphthaletone

Vibronic contributions necessary!

J. Bloino, A. Baiardi, M. Biczysko, *International Journal of Quantum Chemistry* **116**, 1543–1574 (2016), A. Baiardi, J. Bloino, V. Barone, *The Journal of Chemical Physics* **144**, 084114 (2016).

General framework for one-photon spectroscopies

$$I(\omega) = \alpha\omega^{\beta} \sum_{I} \rho_I \sum_{F} \mathcal{F}(\langle \Psi_I | \boldsymbol{P}_{\mathrm{A}} | \Psi_F \rangle, \langle \Psi_F | \boldsymbol{P}^{*}_{\mathrm{B}} | \Psi_I \rangle) \delta(\Delta\omega_{IF} - \omega)$$

- α: constant scalar factor
- β: power, 1 for abs., 3 or 4 for emission
- ω: incident frequency
- ρ_I: Boltzmann population of state I
- Ψ: molecular wavefunction
- $\boldsymbol{P}_{\mathrm{A}}$, $\boldsymbol{P}_{\mathrm{B}}$: spectroscopy-dependent properties, generically labelled $\boldsymbol{P}_{\mathrm{X}}$
- $\Delta\omega_{IF} = |\omega_F - \omega_I|$
- δ: Dirac function, empirically replaced by a broadening function
- $\mathcal{F}$: "interaction" function: real/complex scalar product, summation over Levi-Civita operator, multiple-components combinations

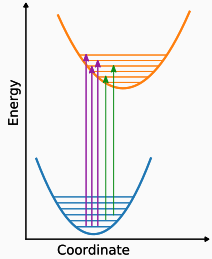
BO, Eckart: $\langle \Psi_I | \boldsymbol{P}_{\mathrm{X}} | \Psi_F \rangle \longrightarrow \langle \psi_I^{\nu} | \langle \phi_I | \boldsymbol{P}_{\mathrm{X}} | \phi_F \rangle | \psi_F^{\nu} \rangle = \langle \psi_I^{\nu} | \boldsymbol{P}^{e}_{\mathrm{X},IF} | \psi_F^{\nu} \rangle$

From abstract implementation to observables

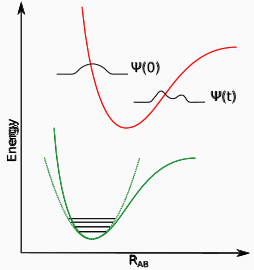
$$\text{TI: } I(\omega) = \alpha\omega^{\beta} \sum_{I} \rho_I \sum_{F} \langle \psi_I^{\nu} \,|\, \boldsymbol{P}^{e}_{\text{A},IF} \,|\, \psi_F^{\nu} \rangle \langle \psi_F^{\nu} \,|\, \boldsymbol{P}^{e}_{\text{B},IF}{}^{*} \,|\, \psi_I^{\nu} \rangle \delta(\Delta\omega_{IF} - \omega)$$

$$\text{TD: } I(\omega) = \frac{\alpha\omega^{\beta}}{Z} \int_{-\infty}^{\infty} dt \; \text{Tr}\left(\boldsymbol{P}^{e}_{\text{A},IF} e^{-\hat{\mathcal{H}}_I \tau_I} \boldsymbol{P}^{e}_{\text{B},IF}{}^{*} e^{-\hat{\mathcal{H}}_F \tau_F} \right) e^{i(\Delta\omega_{IF} - \omega)t}$$

Sum-over-states (time-independent)



Path integral (time-dependent)



From abstract implementation to observables

$$\text{TI: } I(\omega) = \alpha\omega^{\beta} \sum_{I} \rho_I \sum_{F} \langle \psi_I^{v} \,|\, \boldsymbol{P}^{e}_{\text{A,IF}} \,|\, \psi_F^{v} \rangle \langle \psi_F^{v} \,|\, \boldsymbol{P}^{e}_{\text{B,IF}}{}^{*} \,|\, \psi_I^{v} \rangle \delta(\Delta\omega_{\text{IF}} - \omega)$$

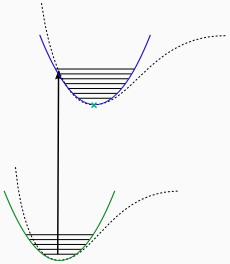
$$\text{TD: } I(\omega) = \frac{\alpha\omega^{\beta}}{Z} \int_{-\infty}^{\infty} dt\ \text{Tr}\left(\boldsymbol{P}^{e}_{\text{A,IF}} e^{-\hat{\mathcal{H}}_I \tau_I} \boldsymbol{P}^{e}_{\text{B,IF}}{}^{*} e^{-\hat{\mathcal{H}}_F \tau_F} \right) e^{i(\Delta\omega_{\text{IF}} - \omega)t}$$

Spec.	I	α	β	$\boldsymbol{P}_{\text{A}}$	$\boldsymbol{P}_{\text{B}}$
OPA	ϵ	$\frac{10\pi N_A}{3\epsilon_0 \ln(10) \hbar c}$	1	$\boldsymbol{\mu}$	$\boldsymbol{\mu}$
OPE	I	$\frac{2N_A}{3\epsilon_0 c^3}$	4	$\boldsymbol{\mu}$	$\boldsymbol{\mu}$
ECD	$\Delta\epsilon$	$\frac{40\pi N_A}{3\epsilon_0 \ln(10) \hbar c}$	1	$\boldsymbol{\mu}$	$\mathfrak{I}(\boldsymbol{m})$
CPL	$\Delta\epsilon$	$\frac{8N_A}{3\epsilon_0 c^3}$	4	$\boldsymbol{\mu}$	$\mathfrak{I}(\boldsymbol{m})$

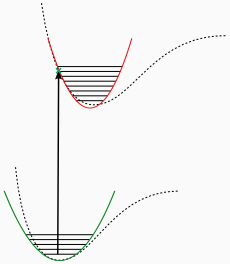
Practical considerations on calculation of $\langle \psi_m^{\nu} \,|\, \boldsymbol{P}_{\mathrm{x}}^{e} \,|\, \psi_n^{\nu} \rangle$

- Relation between basis sets $\longrightarrow$ Duschinsky transformation: $\boldsymbol{Q}_I = \boldsymbol{J}\boldsymbol{Q}_F + \boldsymbol{K}$
- Reference point for description of final-state vibrational wavefunction,

Final-state equilibrium
(Adiabatic)



Initial-state equilibrium
(Vertical)

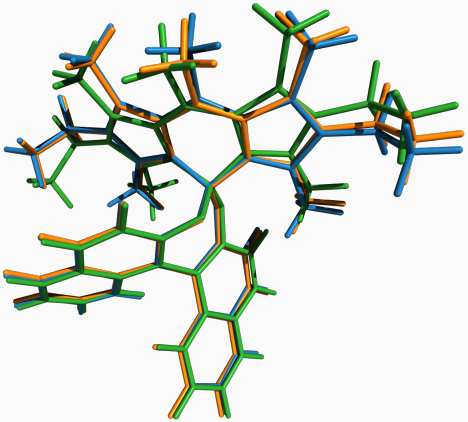


- No analytic expansion of electronic transition moment $\longrightarrow$ Taylor expansion,

$$\boldsymbol{P}_{\mathrm{x}}^{e}(\boldsymbol{Q}) = \boldsymbol{P}_{\mathrm{x}}^{e}(\boldsymbol{Q}^{\mathrm{eq}}) + \sum_i \frac{\partial \boldsymbol{P}_{\mathrm{x}}^{e}}{\partial Q_i} Q_i + \circ(\boldsymbol{Q})$$

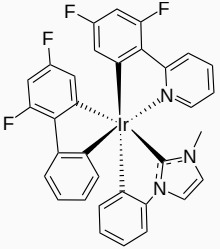
Franck–Condon Herzberg–Teller

Challenges for vibronic calculations

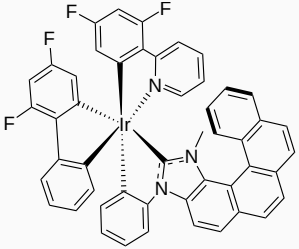


- Large-sized systems
- Molecular flexibility
- Large amplitude motions
- Lack of benchmark including vibronic effects

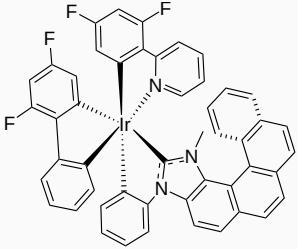
Case studies



Λ-Ir (KA)



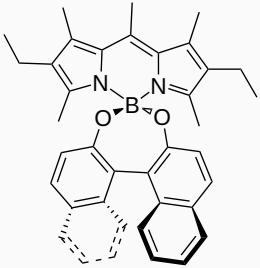
P-Λ-Ir (KC) / M-Δ-Ir



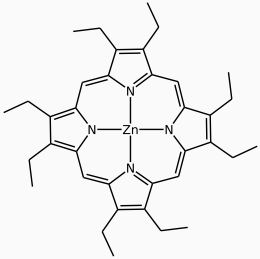
M-Λ-Ir (KD) / P-Δ-Ir

- Multiple sources of chirality ⟶ interference/coordinating effects.
- Scale-up study to calibrate hybrid method for larger systems

Case studies

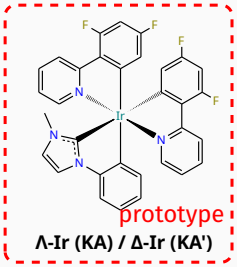


- Spectral energy range spanning large number of electronic states
- Benchmark on vibronic
- Understanding of physico-chemical properties and rationalization of activity

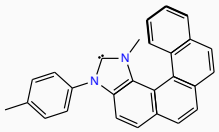


- Rather rigid system with high-symmetry
- Spectral signal strongly modulated by vibronic effects
- Application to MCD and MCPL

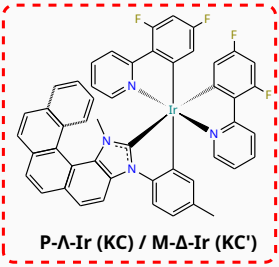
Ir complexes with helicene



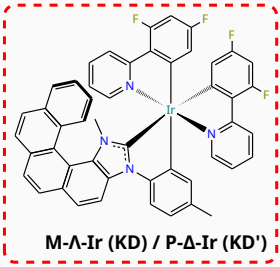
Λ-Ir (KA) / Δ-Ir (KA')



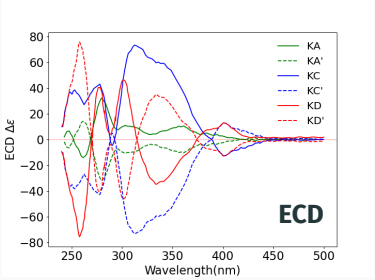
P (KB) / M (KB')

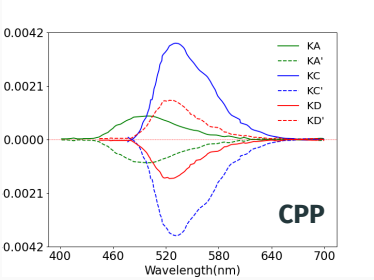


P-Λ-Ir (KC) / M-Δ-Ir (KC')



M-Λ-Ir (KD) / P-Δ-Ir (KD')





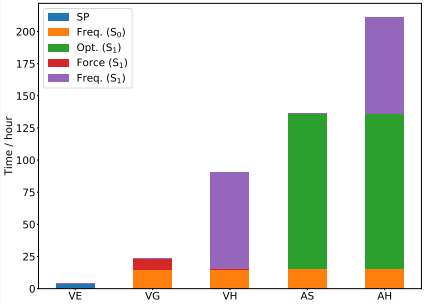
Potential application as

- Biomarker
- Phototherapy
- Light-emitting nodes
- Electrochemical cells

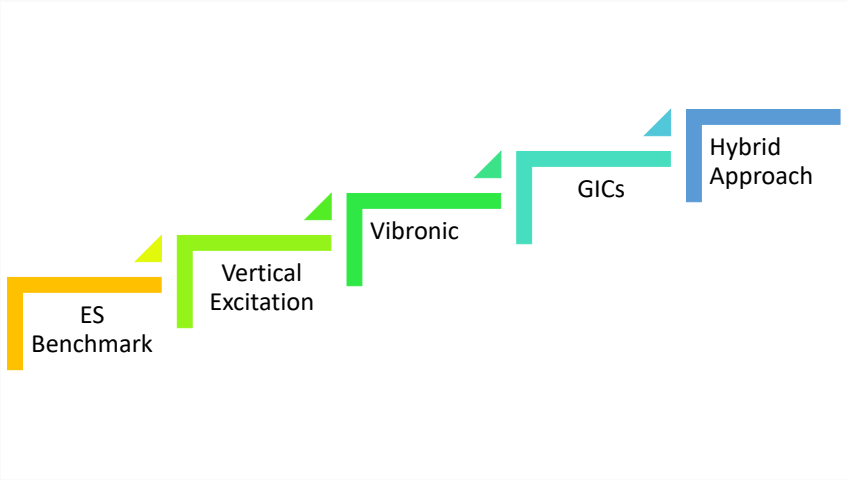
N. Hellou *et al.*, *Angewandte Chemie International Edition* **56**, 8236–8239 (2017).

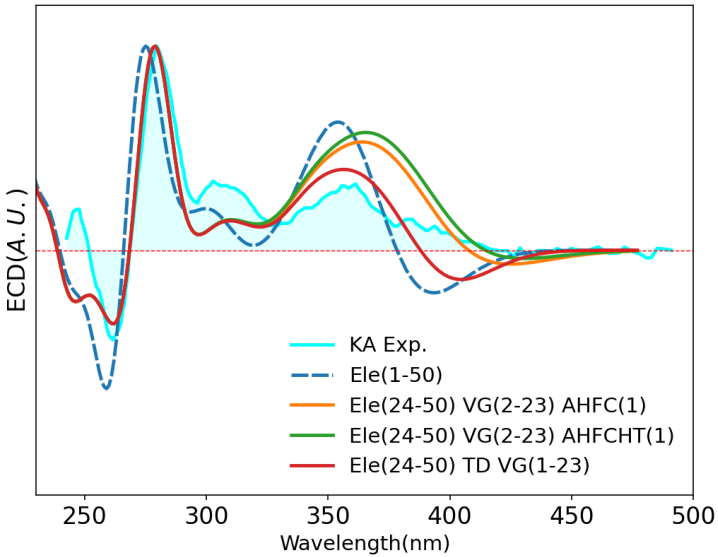
Computational requirements

Quantity	VE	AH	AS	VH	VG	FC	HT
Initial state							
Equilibrium geometry	×	×	×	×	×		
Electronic energy	×	×	×	×	×		
Force constants		×	×	×	×		
Final state							
Equilibrium geometry		×	×				
Electronic energy	×	×	×	×	×		
Energy gradients				×	×		
Force constants		×		×			
Transition moments							
Transition moment	×					×	
First derivative							×



Protocols

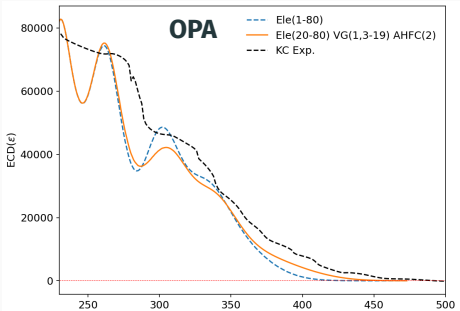

ES
Benchmark
Vertical
Excitation
Vibronic
GICs
Hybrid
Approach

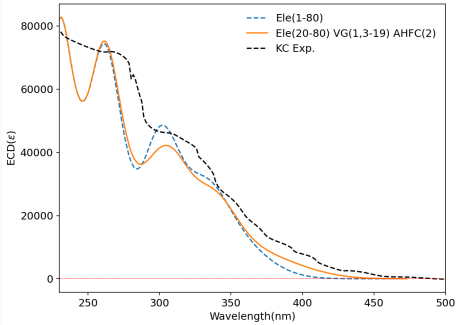

ECD(A. U.)
250
300
350
400
450
500
Wavelength(nm)
KA Exp.
Ele(1-50)
Ele(24-50) VG(2-23) AHFC(1)
Ele(24-50) VG(2-23) AHFCHT(1)
Ele(24-50) TD VG(1-23)

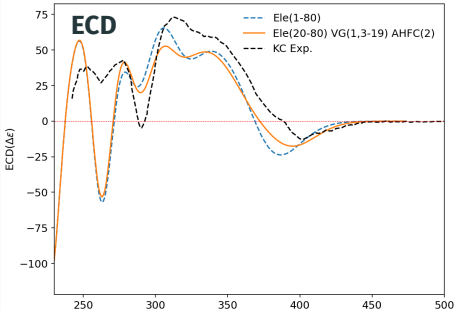
Application to KC and KD

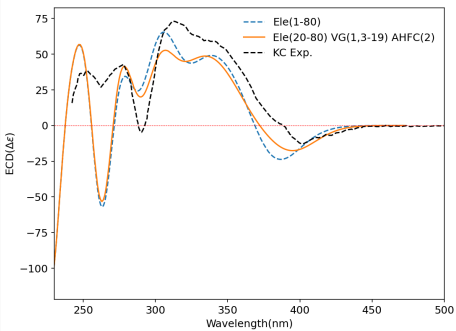
KC

KD

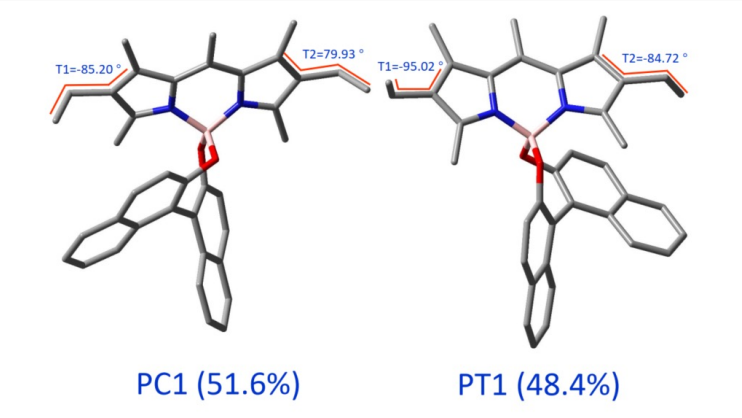








O-BODIPY



Potential applications

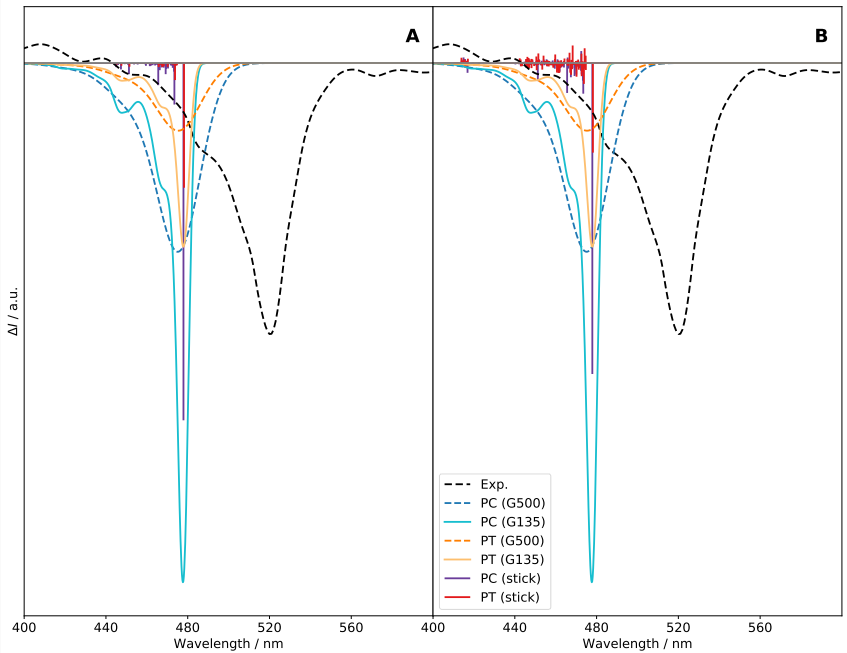
- 3D optical display
- Spintronics

Feature

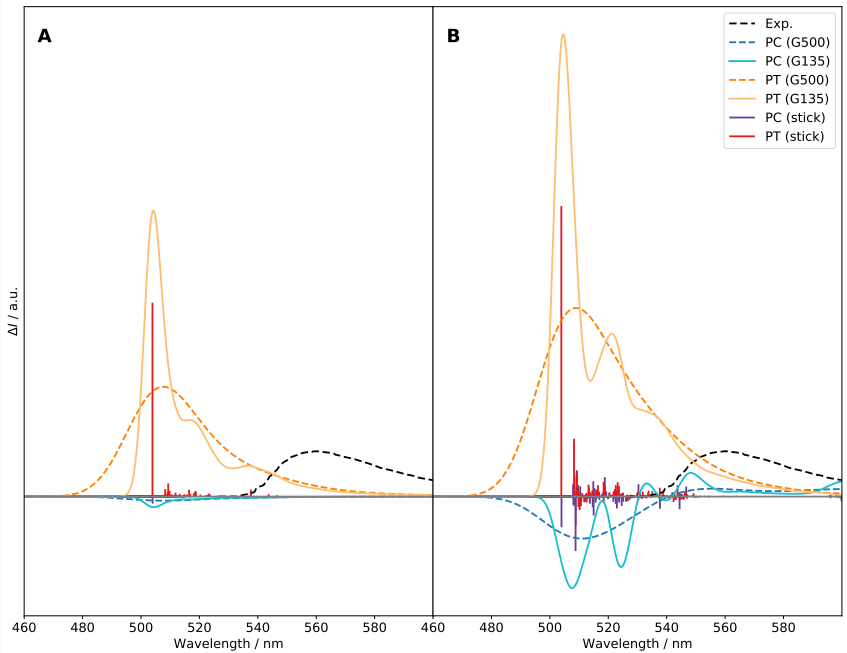
- Tunable properties

E. M. Sánchez-Carnerero *et al.*, *Journal of the American Chemical Society* **136**, 3346–3349 (2014).

O-BODIPY: ECD: spectrum



O-BODIPY: CPL spectrum



O-BODIPY: Results from vibronic calculations

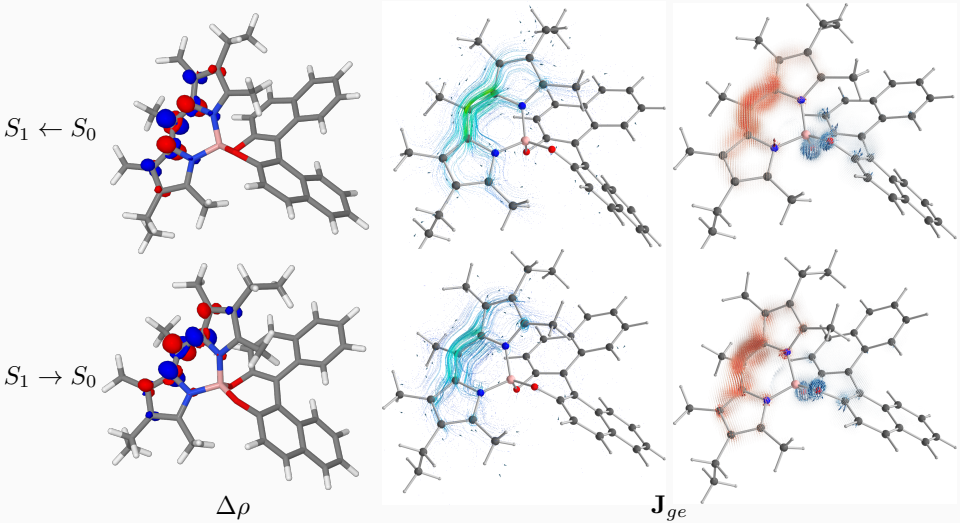
Important discoveries

- Important contribution to ECD spectrum from BINOL moiety
- Strong influence to CPL signal from vibrational modes connecting BODIPY and BINOL units
- ECD signal of trans-conformer 3 times stronger than cis-conformer
- Cancellation of CPL signal caused by cis-conformer
- Results in line with ETCD analysis[1]

[1] ETCD provides physico-chemical insight from intermediate quantities

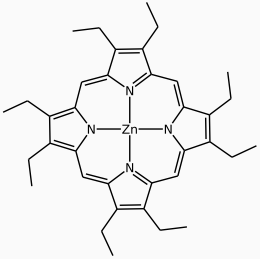
T. B. Freedman *et al.*, *Journal of the American Chemical Society* **119**, 10620–10626 (1997), M. Fusè, F. Egidi, J. Bloino, *Physical Chemistry Chemical Physics* **21**, 4224–4239 (8 2019).

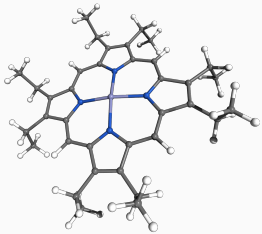
O-BODIPY: ETCD



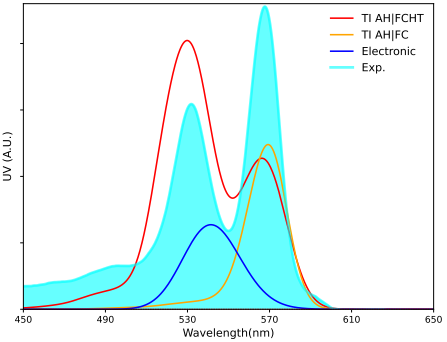
- Contributions to electric dipole as linear patterns of charge flow
- Contributions to magnetic dipole as circular current flow patterns

ZnOEP





26 conformers



Conclusions and perspectives

- Vibronic simulation brings more accurate results and reveal more physical chemical properties.
- Herzberg–Teller term has an obvious effect for ECD at lower energy transitions.
- Hybrid methods are a cost-effective way for medium-large molecular systems.
- General internal coordinates are important factors for flexible groups in large molecule.
- Vibronic properties can provide important insights for better designs of molecular structures.
- More comprehensive studies are necessary to validate theoretical methods and computational protocols.
- Bringing the current machinery to predict vibronic contributions in MCD, MCPL or 2D spectra will allow new interesting applications of technological interests.

Acknowledgements

- Alberto Baiardi (IBM, CH)
- Vincenzo Barone (Scuola Normale Superiore, IT)
- Michael Frisch (Gaussian, US)
- Marco Fusè (U. Brescia, IT)
- Josef Kapitán (Olomouc U., CZ)
- Li Li (Institute of Materia Medica, CN)
- Tao Wu (IOCB, CZ)

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