

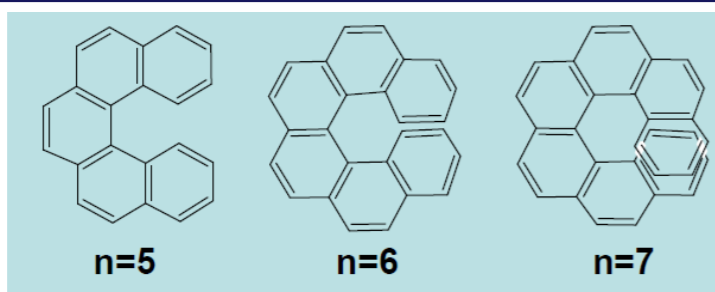
Molecular Spectroscopies of Polycyclic Aromatic Hydrocarbons with a twist: the Helicenes

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HELICENES



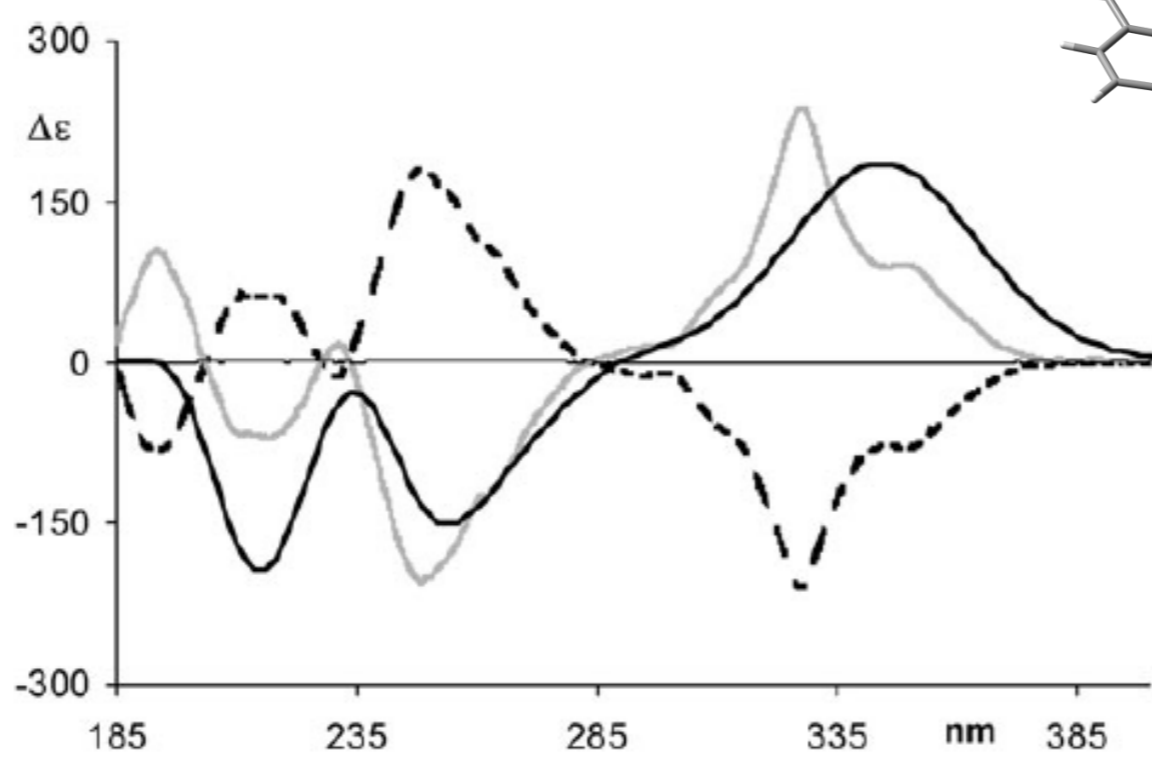
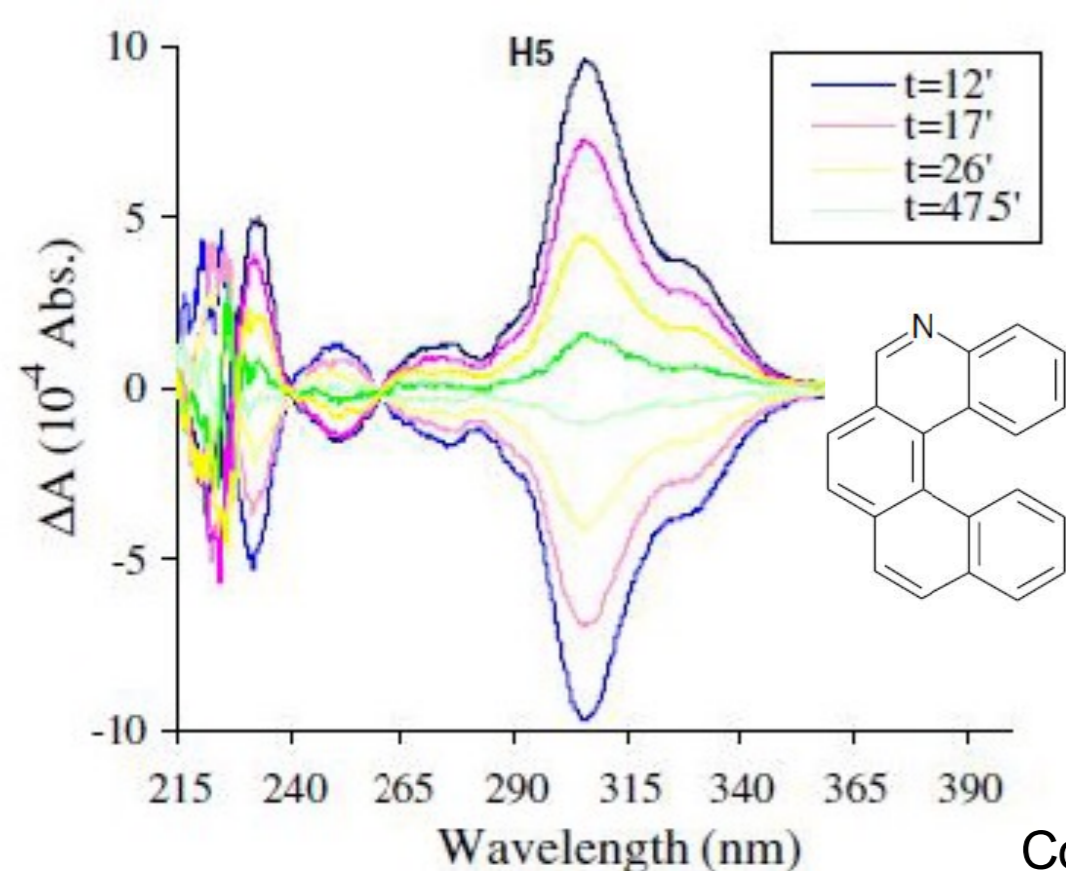
ARE SYSTEMS OF n ORTHO-FUSED BENZENE RINGS ($n=5,6,7$, etc.) POSSIBLY DECORATED OR WITH SIMPLE SUBSTITUTIONS

At Room Temperature: Simple Helicenes with $n=5$ racemize

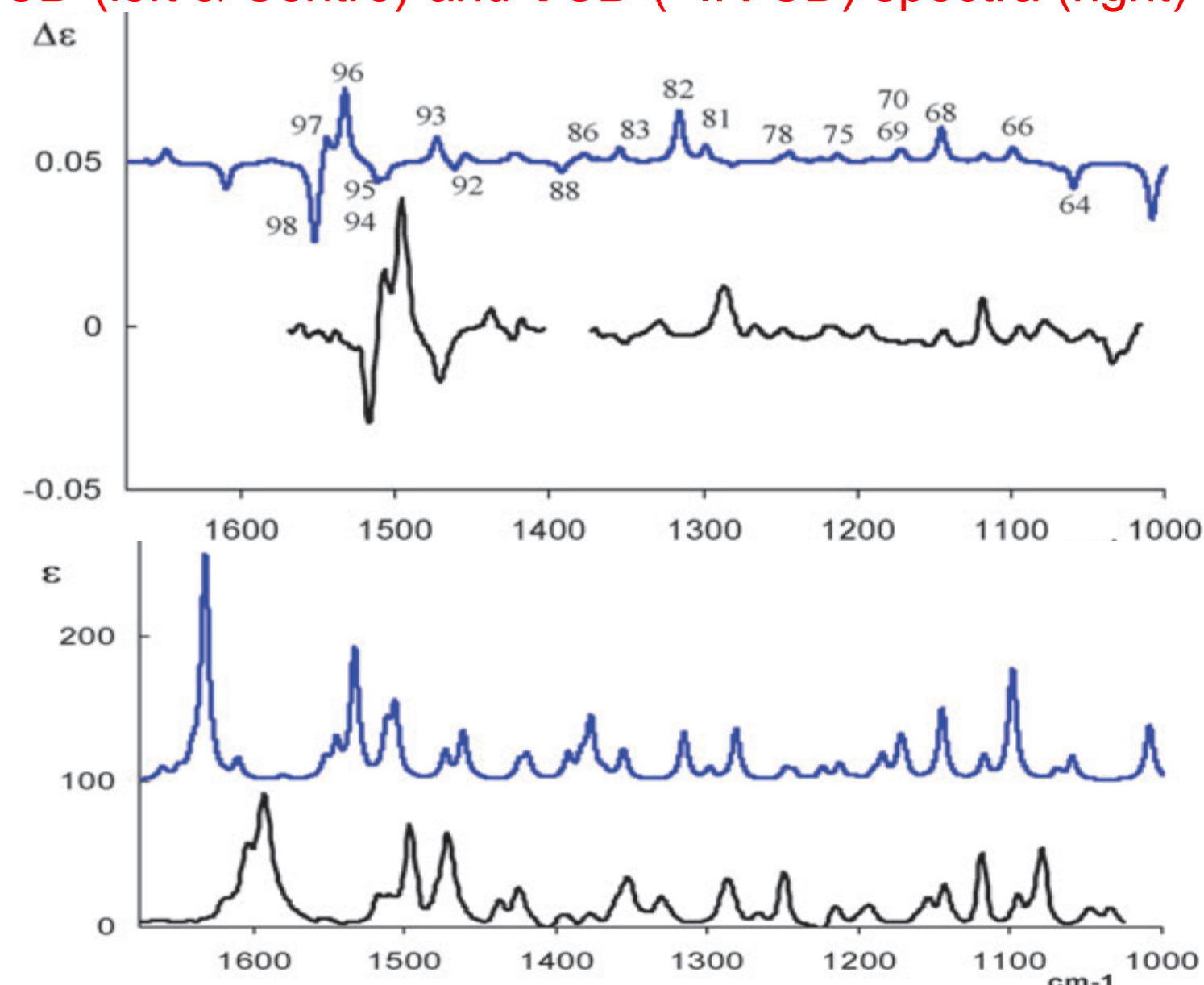
Simple Helicenes with $n \geq 6$ enantiomerically stable

They possess large π -conjugation and large specific optical rotation (for $n=6$, $[\alpha]_D \approx 4000$)

Absolute Configuration established through **ECD** (left & Centre) and **VCD** (=IR-CD) spectra (right)



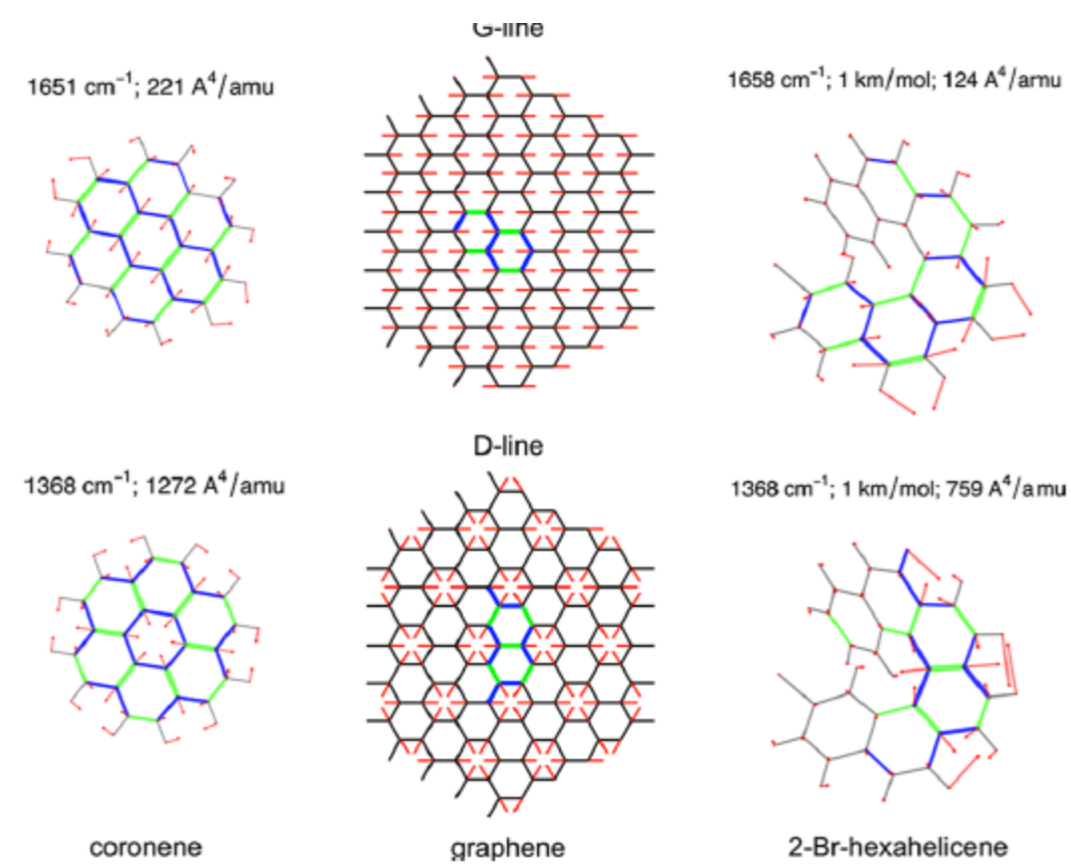
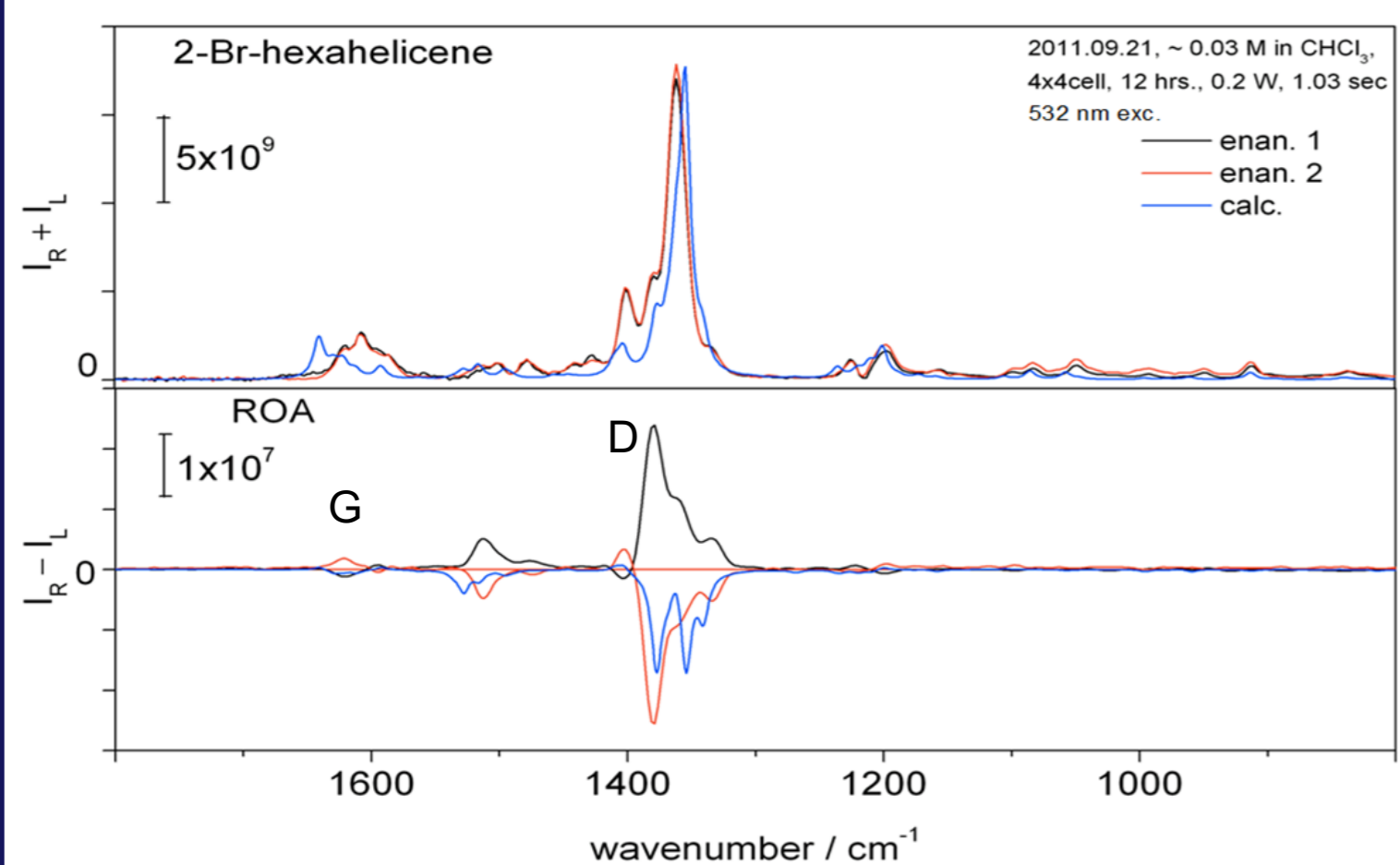
Comparison of calculated ECD spectra (black trace) of P-2-Br-hexahelicene with superimposed experimental ECD spectra of (+)-2-Br-hexahelicene and (-)-2-Br-hexahelicene (grey and dashedline respectively). Phys Chem Chem Phys 2009, 11, 9039-9043



VCD and IR spectra for (-)-2-Br-hexahelicene compared with spectra calculated for M-2-Br-hexahelicene.

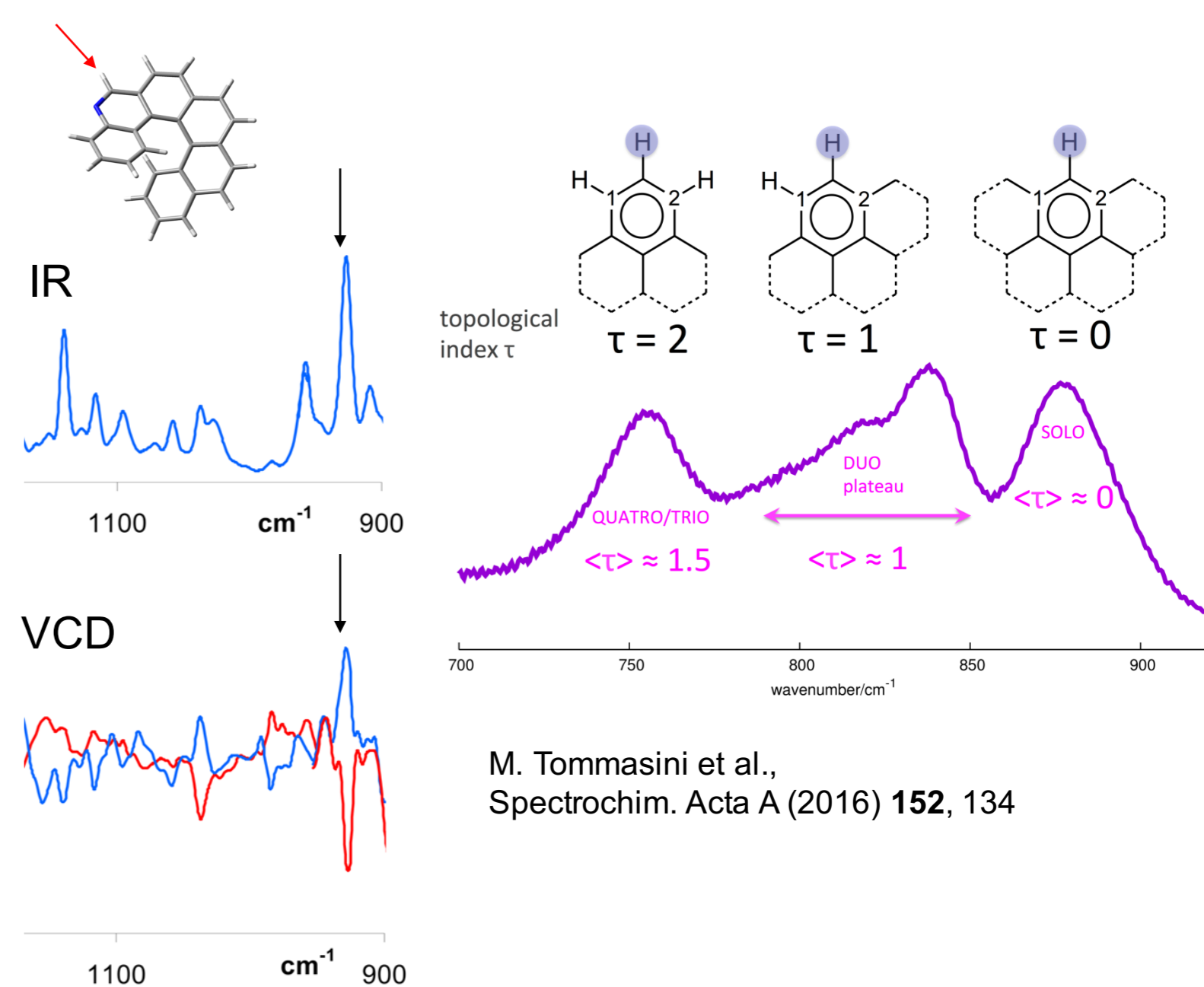
ROA and Raman spectra for (-)-2-Br-hexahelicene

J. Phys. Chem. B 2013, 117, 2221-2230



D and G lines are observed in the Raman spectra of the closest PAH mirror-symmetric analogue, namely Coronene and for Graphene as well. They are quite important in electron-phonon coupling.

IR and VCD fingerprints of the PAH hydrogenated edge: CH out-of-plane bending



M. Tommasini et al., Spectrochim. Acta A (2016) 152, 134

Abbate et al., J. Phys. Chem. C 2014, 118, 1682

Helicenes exhibit also interesting fluorescence phenomena, which have a weak chiral character, when helicenes are simple, or have a strong chiral character when they host hetero-atoms. We monitor this effect by measuring CPL (Circularly Polarized Luminescence) which is opposite for enantiomers.

In the first case CPL bands are substituent sensitive (vibronic origin)

(Abbate et al., J. Phys. Chem. C 2014, 118, 1682)

In the second case CPL is helical sensitive (electronic origin)

(Longhi et al., J. Photobiol. Photochem.: Chemistry 2016, in press)

ECD

CPL

ECD & Absorption

CPL & Fluorescence

