

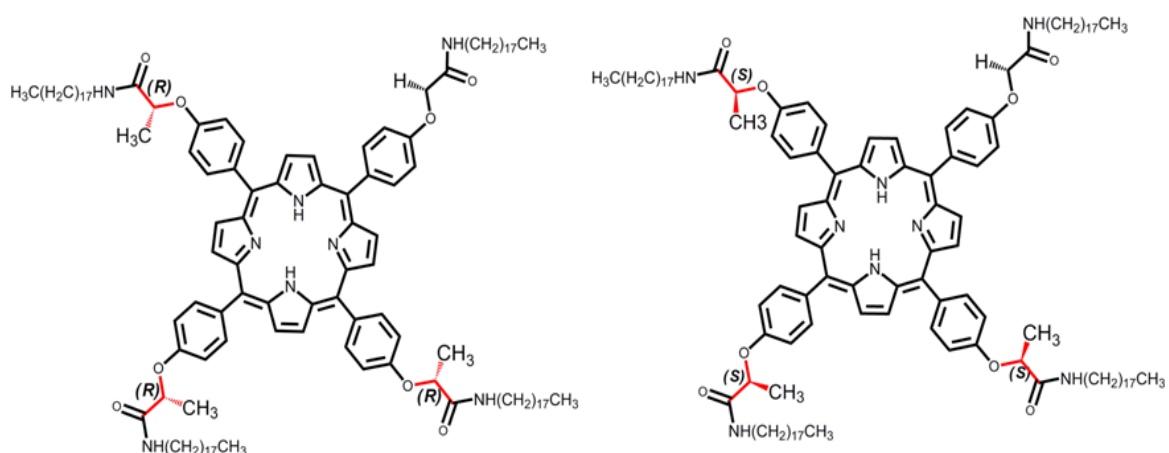
## Electronic Supplementary Information

### Electronic and Vibrational Circular Dichroism Spectroscopies for the Understanding of Chiral Organization in Porphyrin Aggregates

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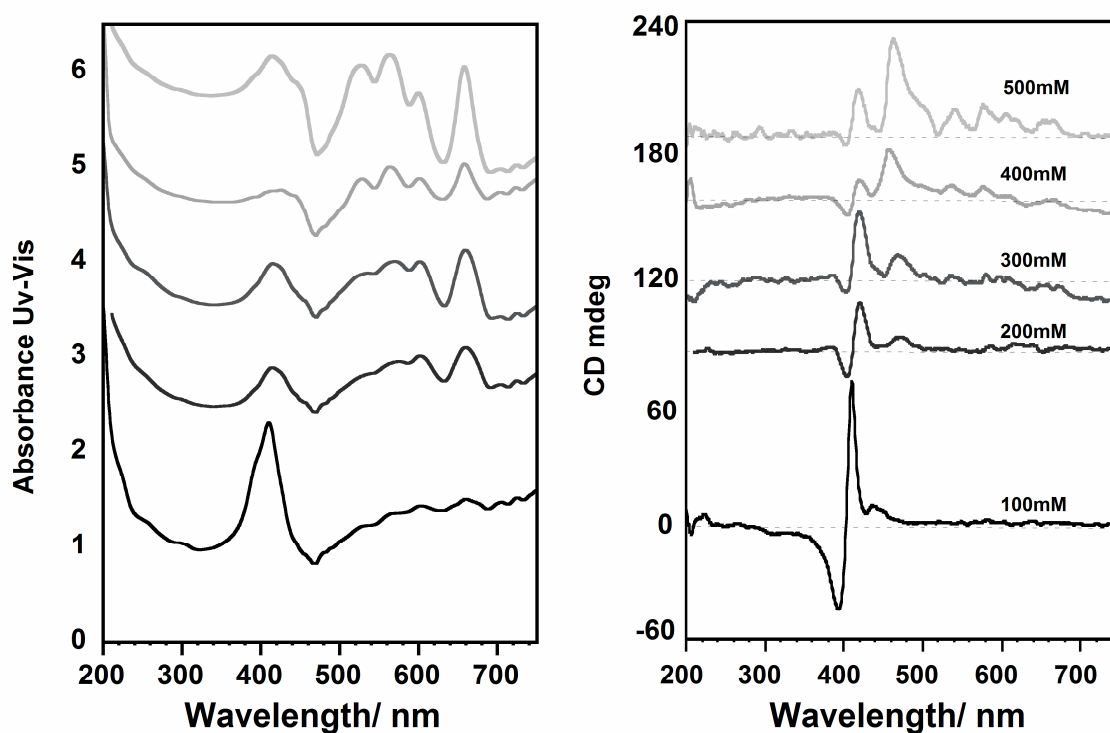
- A. Chemical structure of compound  $(R,R,R)$ -1 and  $(S,S,S)$ -1.
- B. Figures.
- **Figure S1** shows the CD and VCD spectra for the two compounds  $(R,R,R)$ -1 and  $(S,S,S)$ -1.
  - **Figure S2** shows the CD spectra of  $(R,R,R)$ -1 at different concentrations.
  - **Figure S3** shows the dimer model of  $(R,R,R)$ -1.
  - **Figure S4** shows the VCD theoretical spectra of  $(R,R,R)$ -1.
- C. Computational details.
- Molecular Mechanics and Molecular Dynamics
  - CD spectra calculation
  - VCD spectra calculation
- D. Description of the instrumentation
- **Electronic Spectroscopy.**
  - **Vibrational Spectroscopy.**

## A. Chemical Structures

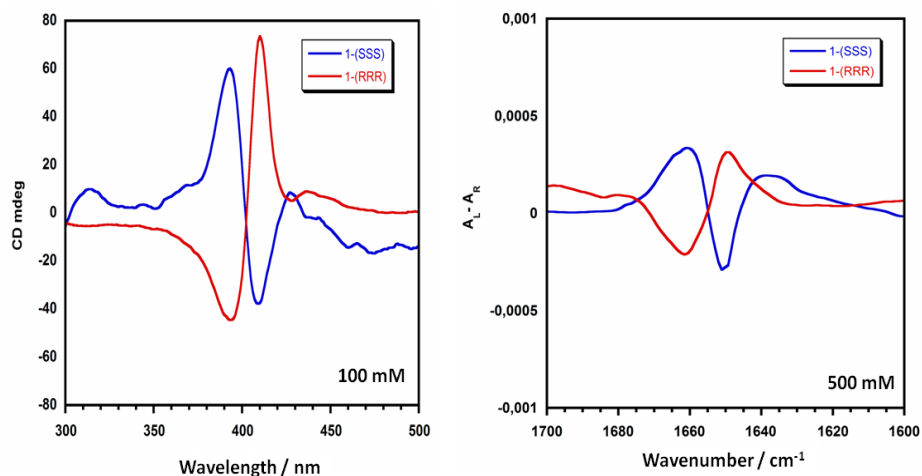


Chemical Structure of Compound (*R,R,R*)-1 (left) and (*S,S,S*)-1 (right).

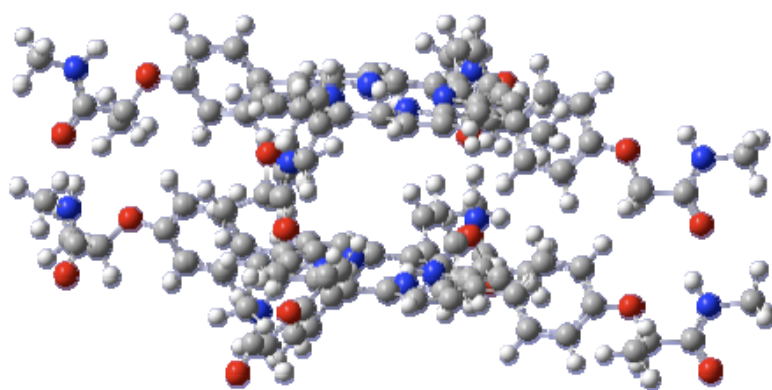
## B. Figures



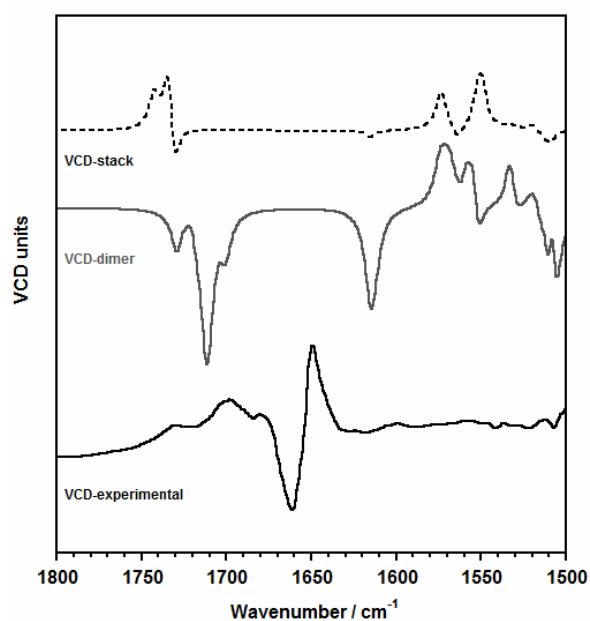
**Figure S1.** UV-Vis absorption spectra (left) and CD spectra (right) of the (*R,R,R*)-1 gels at different concentrations. It is shown how the Qx and Qy bands appear in solutions of increasing concentration.



**Figure S2.** CD (left) and VCD (right) spectra for the two compounds (*R,R,R*)-1 and (*S,S,S*)-1 at 100 mM and 500 mM concentration respectively.



**Figure S3.** Dimer model of (*R,R,R*)-1.



**Figure S4.** Experimental VCD spectrum at room temperature together with the theoretical B3LYP/6-31G VCD spectra for the stacked and dimer conformations of (*R,R,R*)-1.

## C. Computational details.

### Molecular Mechanics and Molecular Dynamics

The self-assembly of *(R,R,R)*-1porphyrins into helical stacks was modelled using the tinker package<sup>1</sup> and the MM3 force-field<sup>2</sup> with periodic boundary condition. Two helices were built: a clockwise helix (CW) and a counter-clockwise (CCW). Considering the C<sub>2</sub> symmetry of the core of the porphyrin, a rotation of 180° is sufficient to reach periodicity. The twist angle between adjacent molecules converge to 2.6°, so 74 molecules are necessary to reach periodicity. The intermolecular distance is about 4.6 Å, resulting in a box of 34.5 nm. To build these helices, we use a random distribution of all the possible situations: chiral centers on top of each other or alternated.

After optimisation the CCW arrangement is more stable than the CW arrangement by 5.0 kcal/mol and per molecule, this difference is coming from the fact that the methyl group on the chiral centres creates a steric hindrance and the formation of hydrogen bonds in the CW helix.<sup>3</sup> Molecular dynamics simulations were performed on the CCW stack in the NVT ensemble at the temperature of 300K during 1 ns. Snapshots extracted from the MD trajectory were used for the CD spectra calculation.

### CD spectra calculation

The calculation of the excitonic CD spectra involves two steps. First, the lowest 20 excited states of the 74 molecules involved in a full turn of the helical structures are computed at the INDO/SCI level (using an active space of 60 occupied and 60 empty molecular orbitals). Then, an excitonic Hamiltonian encompassing a total of 74x20 basis functions (20 localized excitations per molecule) is built on the basis of INDO/SCI<sup>4</sup>excitation energies and exciton couplings. The latter are calculated as Coulomb interactions between transition densities, thus going beyond the usual point dipole model.<sup>5</sup> Diagonalization of this Hamiltonian yields a set of 1480 exciton states  $\alpha$  with energies  $\hbar\omega_\alpha$  and wavefunctions  $|\psi_\alpha\rangle$ , for which the oscillator strength  $f_\alpha$  and the rotational strength  $R_\alpha$  are computed as:<sup>6</sup>

$$f_\alpha = \sum_{i,n} \frac{|\langle \psi_\alpha | \hat{\mu}_{i,n} | G \rangle|^2}{|\underline{\mu}_{i,n}|^2},$$
$$R_\alpha = \frac{\hbar\omega_\alpha}{c} \sum_{i,n} \sum_{j,n'} \frac{\langle \psi_\alpha | \hat{\mu}_{i,n} | G \rangle \times \langle G | \hat{\mu}_{j,n'} | \psi_\alpha \rangle \cdot (\underline{r}_n - \underline{r}_{n'})}{|\underline{\mu}_{i,n}| |\underline{\mu}_{j,n'}|},$$

where  $c$  is the speed of light,  $\mu_{i,n}$  the transition dipole moment from the ground state  $|g\rangle$  to the excited state  $|i\rangle$  of molecule  $n$  along the stack,  $\hat{\mu}_{i,n} = \mu_{i,n} (|i,n\rangle\langle g| + h.c.)$  the corresponding dipole operator,  $|G\rangle$  the ground state of the helical stack (product state of all  $|g\rangle$ ), and  $|\psi_\alpha\rangle = \sum_{i,n} c_{i,n}^\alpha |i,n\rangle$  the exciton state wavefunctions expanded in terms of the  $c_{i,n}^\alpha$  eigenvectors.

The absorption/CD response at input frequency  $\omega$  is calculated on the basis of the oscillator/rotational strengths as:

$$Abn(\omega) = \langle \sum_{\alpha} f_{\alpha} G(\omega - \omega_{\alpha}) \rangle ,$$
$$CD(\omega) = \langle \sum_{\alpha} R_{\alpha} G(\omega - \omega_{\alpha}) \rangle ,$$

where  $G(\omega - \omega_{\alpha})$  is a Gaussian function centred around  $\omega_{\alpha}$  with variance  $\sigma = 0.1$  eV. The brackets denote a configurational average over the positional and energetic disorder as explored during the MD simulations. Here, a total of 17 supramolecular helical structures, each consisting of 74 molecules, were used; this approach was found to yield CD spectra that are stable with respect to configurational averaging.

### VCD spectra calculation

We choose to perform the VCD calculations on two different systems: a monomer and a dimer extracted from the MM calculation. In both cases, we replaced the long alkyl chains by a methyl group to save computational time. The monomer and the dimer were reoptimized and the VCD spectra were calculated at the B3LYP/6-31g(d) level of theory using the Gaussian 09 program.<sup>7</sup>

## D. Description of the instrumentation

**Electronic Spectroscopy.** CD and UV-Vis spectra were recorded on a Jasco 815 spectropolarimeter. Room temperature spectra from 200 to 800 nm were achieved from one solution of (*R,R,R*)-**1** or (*S,S,S*)-**1** at the indicated concentration. The electronic spectra were recorded sequentially to the IR and VCD spectra in all the case. The following parameters were applied: scan speed: 100 nm/min, spectral resolution: 4 cm<sup>-1</sup> and response time of 4 s, while the spectrometer was continuously purged with dry N<sub>2</sub> gas. Final spectra were obtained as the average of a minimum of ten scans.

**Vibrational Spectroscopy.** Infrared spectra were recorded at room temperature using a Bruker Vertex 70 Fourier transform (FT) spectrometer purged with dry N<sub>2</sub> gas. Typically, 54 scans at a resolution better than 4 cm<sup>-1</sup> were accumulated to optimize the signal-to-noise ratio. Individual scans were examined by the recording routine before averaging, being automatically discarded when the mean intensity deviations were greater than 10% over the full interferogram length.

VCD spectra were measured with a Bruker PMA50 optical bench coupled to a Vertex 70 spectrometer. In the PMA50, the infrared radiation is focused by a BaF<sub>2</sub> lens, passing an optical filter (3800-600 cm<sup>-1</sup> range) and a ZnSe photoelastic modulator (PM, 50 kHz frequency). The light beam is finally collected by a D313/QMTC detector with nondichroic BaF<sub>2</sub> windows. A previous calibration of the PM at a fixed wavenumber is required before recording a VCD spectrum. A spectral region of 600 cm<sup>-1</sup> is then available centered on each calibration wavenumber. Typically, calibrations at 1500 cm<sup>-1</sup> allowed us to obtain a VCD signal over the whole infrared region which is interested for us. Every VCD spectrum was the result of averaging a minimum of 12000 scans (9 h acquisition times) at a spectral resolution of 4 cm<sup>-1</sup>. VCD and IR spectra were recorded at the same time.

FT Raman scattering spectra were collected on a Bruker FRA 106/S apparatus with a Nd:YAG laser source ( $\lambda_{exc}$ =1064 nm) in a backscattering configuration. Samples were analyzed as solution of (*R,R,R*)-**1** or (*S,S,S*)-**1** at the indicated concentration, and 1000 scans were averaged with a spectral resolution of 2 cm<sup>-1</sup>.

Measurement and treatment of the vibrational spectra were carried out using the OPUS 6.5 © spectroscopic software.

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<sup>2</sup> N. L. Allinger, Y. H. Yuh, J. H. Lii, *J. Am. Chem. Soc.* 1989, **111**, 8551–8566.

<sup>3</sup> P. Iavicoli, H. Xu, L.N. Feldborg, M. Linares, M. Paradinas, S. Stafström, C. Ocal, B. Nieto-Ortega, J. Casado, J. T. López Navarrete, R. Lazzaroni, S. de Feyter, D. B. Amabilino. *J. Am. Chem. Soc.* 2010, **132**, 9350-9362.

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<sup>6</sup> F.C. Spano, S.C.J. Meskers, E. Hennebicq, and D. Beljonne, *J. Am. Chem. Soc.* 2007, **129** 7044-7054.

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<sup>7</sup> Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.