Tunable Supramolecular Chirogenesis in the Self-Assembling of Amphiphilic Porphyrin-Amine systems.



Scheme S1. i) EDCl, HOBT, dry CH₂Cl₂, 0°C, 1h; then RT, 48 h. ii) TFA/CH₂Cl₂ (2/3, v/v), 1.5 h, then aqueous NaHCO₃. iii) Zn(OAc)₂·2H₂O, CHCl₃/MeOH, RT, 1h. Metalation, and subsequent treatment of **pCTPP** (Zn(OAc)₂·2H₂O, CHCl₃/MeOH, rt, 1h; then aqueous NaHCO₃) afforded **ZnpCTPP(-)**. Spectroscopic and analyutical data were in full agreement to those reported in literature. See reference: Chouikrat, R., Champion, A., Vanderesse, R., Frochot, C., Mussaron, A. *J. Porphyrins Phthalocyanines*. 2014, **18**, 1-6.



Figure S1. CD spectra of equilibrium solutions (5 μM; EtOH/H₂O 25/75 v:v; 298 K) of: (A) **(D)ZnP(-)** in the presence of **(R)-1-phenyl-ethanamine** (black trace), **(S)-1-phenyl-ethanamine** (red trace). (B) **(L)ZnP(-)** in the presence of **(R)-1-phenyl-ethanamine** (black trace), **(S)-1-phenyl-ethanamine** (red trace).



Figure S2. UV-Vis (A) and CD spectra (B) of the aggregates of **(D)ZnP(-)** (5 μ M; EtOH/H₂O 25/75 v:v; 298 K) in the presence of achiral benzylamine (5.0 × 10⁻⁴ M) at t = 0 (black traces), and at equilibrium (red traces).



Figure S3. (A) UV-Vis spectral variations with time of **(L)ZnP(-)** (5 μ M; EtOH/H₂O 25/75 v:v; 298 K) in the presence of (R)-1-phenyl-ethanamine (5.0 × 10⁻⁴ M). (B) Corresponding kinetic plot (λ = 422 nm).



Figure S4. (A) UV-Vis spectral variations with time of **(L)ZnP(-)** (10 μ M; EtOH/H₂O 25/75 v:v; 298 K) in the presence of (R)-1-phenyl-ethanamine (1.0 x 10⁻³ M). (B) Corresponding CD plot at λ = 451 nm (black circles) and λ = 439 nm (red circles).



Figure S5. SEM topographies of precipitates from 10 μM equilibrium solutions of **(D)ZnP(-)** (A) and **(L)ZnP(-)** (B) in the presence of **(S)-1-phenylethanamine**.



Figure S6. (A) Microscope transmission images of drop casted equilibrium solution on glass of (A) (*D*)**ZnP(-)@**(*R*)**-1-phenylethanamine** solution, and corresponding fluorescence emission image, evidencing the quenching of fluorescence of the sample.

	Crossover wavelength, nm	
Porphyrin	Вн	B_J
(D)ZnP(-) ^(a)	420 (+ /-)	442 (-/+)
(L)ZnP(-) (a)	421 (-/+)	441 (+/-)
(D)ZnP(-)@(R)-amine	423 (+/-)	431; 443 (-/+/-)
(D)ZnP(-)@(S)-amine	423 (b)	432; 444 (+/-/+)
(L)ZnP(-)@(R)-amine	424 (-/+)	433; 446 (-/+/-)
(L)ZnP(-)@(S)-amine	424 (b)	431; 442 (+/-/+)
ZnpCTPP(-)@(R)-amine	-	433 nm (-/+)
ZnpCTPP(-)@(S)-amine	-	433 nm (+/-)

Table 1. Spectroscopic parameters for the CD spectra of porphyrin aggregates (EtOH/H₂O 25/75 % (v:v) at 5.0 μ M, 298 K) in the presence of 5.0 x 10⁻⁴ M of (R)- or (S)-1-phenylethanamine (amine). The uncertainties of the values are within ± 1 nm.

(a) Experiment carried out in the absence of amine; see reference 29. ^(b) The sign of the couplet of the B_H band could not be ascertained with accuracy due to partial overlap to the more intense B_I transition.