Supporting Information

Induction of Supramolecular Chirality in Di-Zinc(II) Bisporphyrin *via Tweezer* Formation: Synthesis, Structure and Rationaliztion of Chirality

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Instrumentation

Elemental (C, H, and N) analyses were performed on a CE-440 elemental analyzer. ^{1}H NMR spectra were recorded on a JEOL 500 MHz instrument. The residual ^{1}H resonances of the solvents were used as a secondary reference. UV-vis and CD-spectra were recorded on a Perkin-Elmer UV-vis and a JASCO J-815 spectrometer, respectively.

X-ray Structure Solution and Refinement. Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low-temperature apparatus and intensity data were collected using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). The data integration and reduction were processed with SAINT[1] software. An absorption correction was applied.[2] The structure was solved by the direct method using SHELXS-97 and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97 program package.[3] Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using SHELXL default parameters.

Experimental Section

Materials:

The synthesis of **1** is accomplished by following the literature methods[4]. Reagents and solvents are purchased from commercial sources and purified by standard procedures before use.

Synthesis of **1**·DPEA:

1 (50mg, 0.039 mmol) was dissolved in 2.5mL of distilled dichloromethane. (1*R*,2*R*)-DPEA (9.9 mg, 0.047 mmol) was added to it and stirred for about 15 min. The resulting solution was then filtered off to remove any solid residue and carefully layered with cyclohexane. On standing for 6-7 days in air at room temperature, dark crystalline solid were precipitated out which was then isolated by filtration, washed well with cyclohexane and dried in vacuum. Yield: 44 mg (75%). Anal. Calcd (found): C, 74.04 (74.15); H, 6.49 (6.55); N, 9.60 (9.69) UV-vis (Chloroform) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 412(2.47 x 10^5), 429^{sh}(5.39 x 10^4), 543(2.44 x 10^4), 577(1.77 x 10^4). ^{1}H NMR ($CDCl_3$, 218 K): 10.07 (*s*, 2H, 10-meso-*H*); 10.03 (*s*, 2H, 15-meso-*H*);

10.01 (*s*, 2H, 20-meso-*H*); 8.05 (*d*, 1H, Ar-*H*); 7.81 (*d*, 1H, Ar-*H*); 7.69 (*m*, 2H, Ar-*H*); 7.29 (*d*, 2H, Ar-*H*); 7.07 (*t*, 1H, Ar-*H*); 6.91 (*br*, 1H, Ar-*H*); 6.74 (*m*, 2H, -C*H,* DPEA); 6.60 (*m*, 4H, -C*H,* DPEA); 5.31 (*m*, 4H, -C*H,* DPEA); 4.08-3.61 (*m*, 16H, -CH_2); 2.69-0.80 (*m*, 48H, -CH_3); -0.62 (*br*, 2H, -C*H,* DPEA); -1.60 (*br*, 4H, -C*H*, DPEA).

Synthesis of **1**·CHDA:

1 (50mg, 0.039 mmol) was dissolved in 2.5mL of distilled dichloromethane. (1*S*,2*S*)-CHDA (5.4 mg, 0.047 mmol) was added to it and stirred for about 10 min. The resulting solution was then filtered off to remove any solid residue and carefully layered with cyclohexane. On standing for 6-7 days in air at room temperature, dark crystalline solid were precipitated out which was then isolated by filtration, washed well with cyclohexane and dried in vacuum. Yield: 45 mg (82%). Anal. Calcd (found): C, 72.32 (72.23); H, 6.81 (6.92); N, 10.29 (10.33) UV-vis (Chloroform) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 412(3.45 x 10^5), 429^{sh}(7.87 x 10^4), 546(2.45 x 10^4), 580(1.39 x 10^4). ^{1}H NMR ($CDCl_3$, 295K): δ 10.04 (*s*, 2H, 10-meso-*H*); 9.83 (*s*, 2H, 15-meso-*H*); 9.43 (*s*, 2H, 20-meso-*H*); 8.58 (*d*, 1H, Ar-*H*); 8.16 (*d*, 1H, Ar-*H*); 7.96 (*t*, 1H, Ar-*H*); 7.92 (*t*, 1H, Ar-*H*); 7.76 (*t*, 1H, Ar-*H*); 7.15 (t, 1H, Ar-*H*); 7.08 (*d*, 1H, Ar-*H*); 6.99 (*d*, 1H, Ar-*H*); 3.96-2.93 (*m*, 16H, -CH_2); 1.85-1.04 (m, 48H, -CH_3); -0.75, (*m*, 2H, CHDA); -2.33 (*m*, 2H, CHDA); -3.50 (*m*, 2H, CHDA); -6.42 (*m*, 2H, CHDA); -7.05 (*m*, 2H, CHDA); -7.91 (*m*, 4H, -NH_2).

Binding constant determination:

The binding constants between **1** and (1*R*,2*R*)-DPEA are determined by UV-vis spectroscopic titration method. The addition of ligand (10^{-6} to 10^{-3} M) to chloroform solution of **1** ($4x10^{-6}$M) at 295K primarily results red shift of Soret band (393 to 412 nm) along with shoulder at 429 nm and Q-band (536 to 543, 571 to 577 nm). The nonlinear least-square curve-fitting of the absorption spectral data at 412 nm for 1:1 complexation was obtained by applying Equation (1)[5] in which A_0, and A_∞ are absorbances of **1** and **1**·DPEA respectively, and [L] is the concentration of guest added.

$$A = (A_0 + K_a[L]A_\infty)/(1 + K_a[L]) \qquad (1)$$

When absorbance, A is plotted against concentration of ligand, [L], K_a is obtained by nonlinear curve-fitting as shown. The binding constant at 295 K is found to be $1.7 \times 10^3 M^{-1}$.

The binding constant between **1** and (1*S*,2*S*)-CHDA are also determined by UV-vis spectroscopic titration method. The addition of (1*S*,2*S*)-CHDA (10^{-6} to 10^{-5} M) to chloroform solution of **1** (1×10^{-6}M) at 295K which results red shift of Soret band (393 to 412 nm) along with shoulder at 429 nm and Q-band (536 to 546, 571 to 580 nm). The nonlinear least-square curve-fitting of the absorption spectral data at 412 nm for 1:1 complexation was obtained by applying Equation (1). K_a is found to be $1.6 \times 10^5 M^{-1}$.

References:

1) *SAINT*+, 6.02 ed.; Bruker AXS, Madison, WI, 1999.
2) G. M. Sheldrick, SADABS 2.0, 2000.
3) G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

4) M. Tanaka, K. Ohkubo, C. P. Gros, R. Guilard and S. Fukuzumi, *J. Am. Chem. Soc*., 2006, **128**, 14625.

5) S. Fukuzumi, Y. Kondo, S. Mochizuki and T. Tanaka, *J. Chem. Soc. Perkin Trans II*, 1989, 1753.

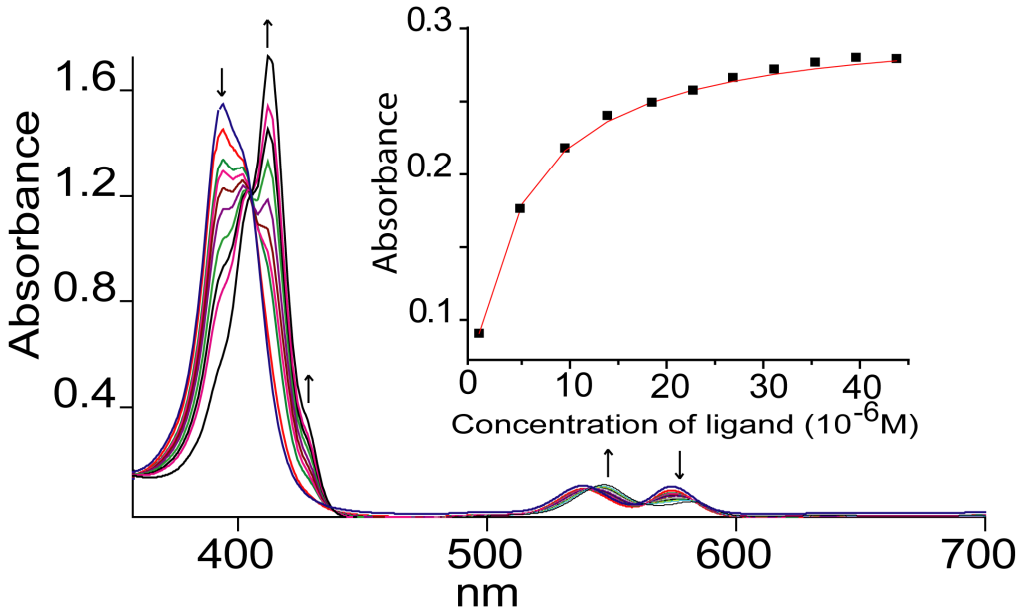

Figure S1: UV-visible spectral changes of **1** in chloroform upon addition of (1*S*,2*S*)-CHDA as the host: guest molar ratio changes from 1:0 to 1:45 at 295K. Inset shows the change of absorbance at 412 nm**. S**olid line represents non-linear least square fit for 1:1 complexation.

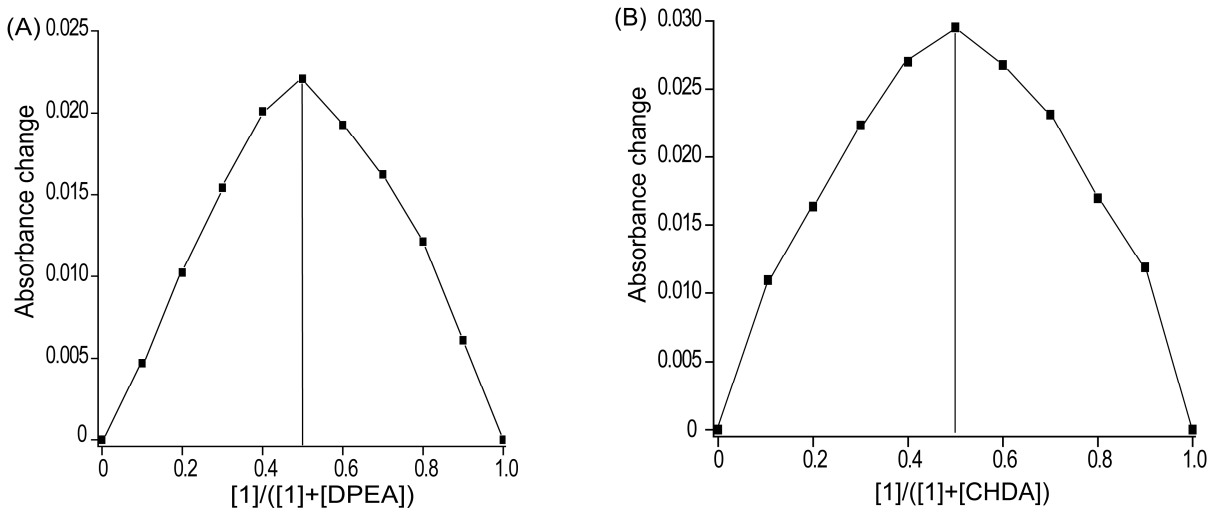

Figure S2: Job's plot monitored at 412 nm establishing the 1:1 stoichiometry for the binding of (A) (1*R*,2*R*)-DPEA and (B) (1*R*,2*S*)-CHDA with the host molecule **1** in chloroform at 295 K.

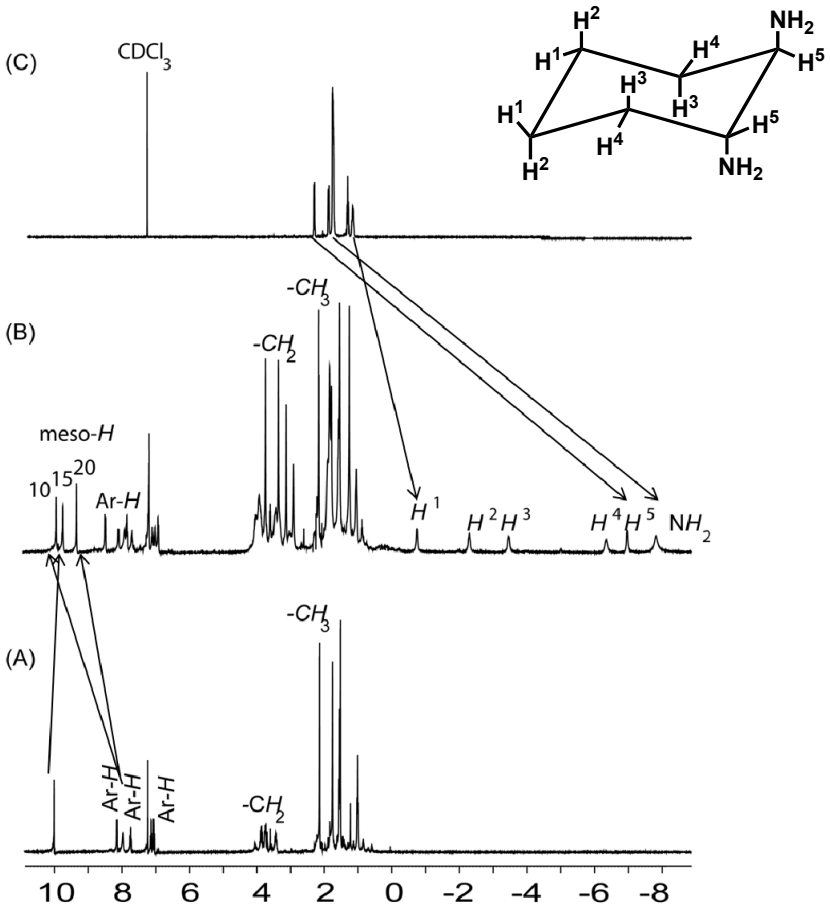

Figure S3. ^{1}H NMR spectra of (A) **1**, (B) **1**•CHDA and (C) (1*S*,2*S*)-CHDA at 295 K in $CDCl_3$. Inset shows the proton numbering scheme of CHDA ligand.

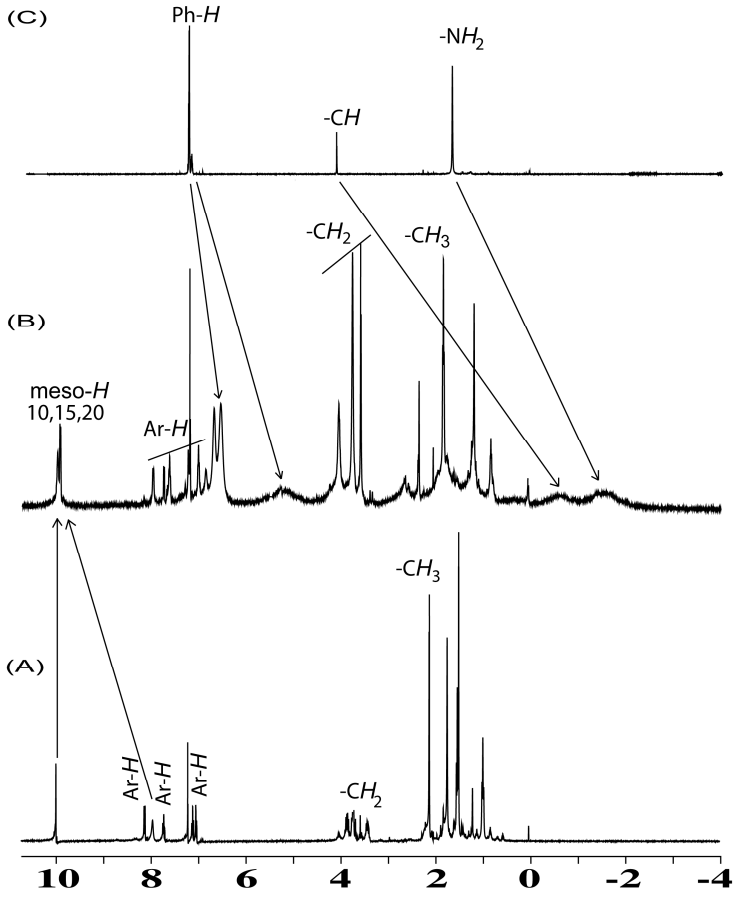

Figure S4. ^{1}H NMR spectra of (A) **1**, (B)**1**•DPEA and (C) (1*R*,2*R*)-DPEA at 218 K in $CDCl_3$.

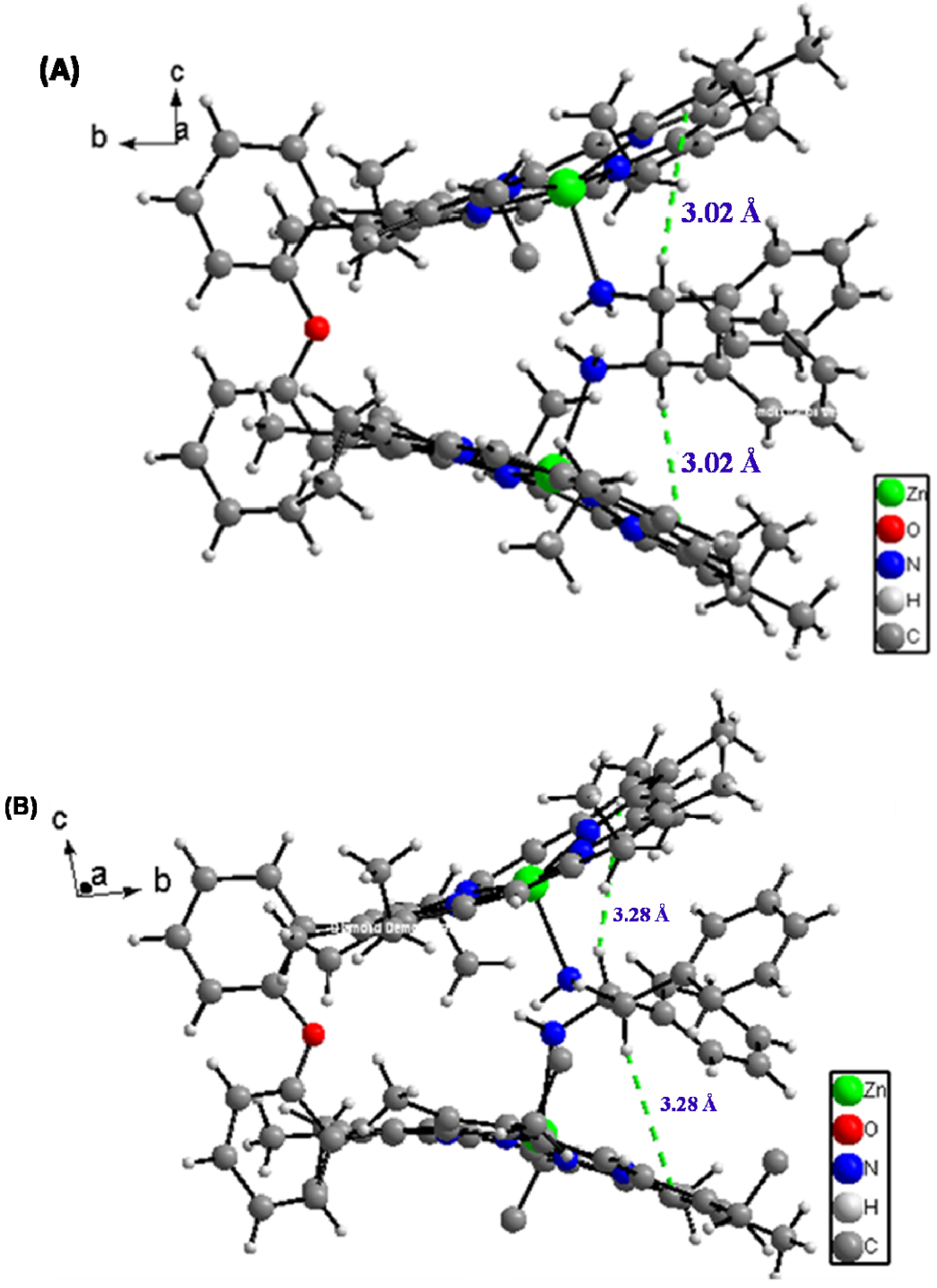

Figure S5. CH-π interactions of ligand hydrogens with the porphyrin pyrrole rings in **1**•DPEA; (A) right-handed screw and (B) left-handed screw.

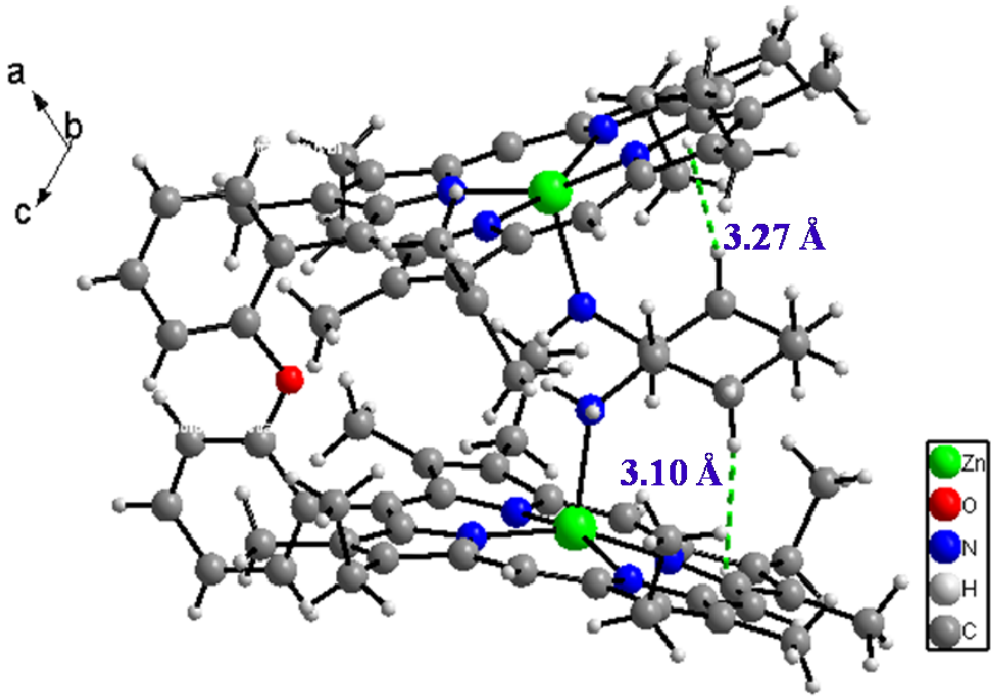

Figure S6. CH-π interaction of ligand hydrogens with the porphyrin pyrrole rings in **1**•CHDA.

Table S1: UV-vis and CD spectral data in chloroform at 295 K.

Complex	UV-vis, λ (nm) B transitions	CD data, λ (nm) [Δε ($M^{-1}cm^{-1}$)]		
		First cotton	Second cotton	A_{obs} [a]
1•DACH	412, 429(sh)	429[+310]	412[-205]	+515
1•DPEA	412, 429(sh)	429[+49]	412[-23]	+72

[a] A_{obs} (= $\Delta\varepsilon_1$- $\Delta\varepsilon_2$) represents the total amplitude of the experimentally observed CD couplets.