Supporting Information

Unprecedented Phthalocyanines Bearing Eight Di-butylamino Peripheral Substituents: Synthesis, Spectroscopy, and Structure

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Scheme S1. Synthesis of **1**-**4**.

Figure S1. Experimental and simulated isotopic patterns for **1**-**4**.

Figure S2. ^{1}H NMR spectrum of **2** recorded in $CDCl_3$/[D_5]pyridine (v/v = 150:1) at 25°C.

Figure S3. ^{1}H NMR spectrum of **4** recorded in $CDCl_3$ at 25°C.

Figure S4. Electronic absorption spectra of M{Pc[N(C_4H_9)$_2$]$_8$} (M = 2H, Mg, Cu, Zn) (**1**-**4**) in $CHCl_3$.

Figure S5. IR spectra of M{Pc[N(C_4H_9)$_2$]$_8$} (M = 2H, Mg, Cu, Zn) (**1**-**4**).

Figure S6. Cyclic voltammograms of **1**-**4** (from top to bottom) in CH_2Cl_2/pyridine (50:1) containing 0.1 mol dm^{-3} [Bu_4N][ClO_4] at a scan rate of 30 mV s^{-1}.

Figure S7. The two adjacent H_2{Pc[N(C_4H_9)$_2$]$_8$} (**1**) molecules and 1-D supramolecular structure of **1**.

Figure S8. The three dimensional structure of H_2{Pc[N(C_4H_9)$_2$]$_8$} (**1**).

Figure S9. The two adjacent Zn{Pc[N(C_4H_9)$_2$]$_8$} (**4**) molecules and 1-D supramolecular structure of **4**.

Figure S10. The three dimensional structure of Zn{Pc[N(C_4H_9)$_2$]$_8$} (**4**).

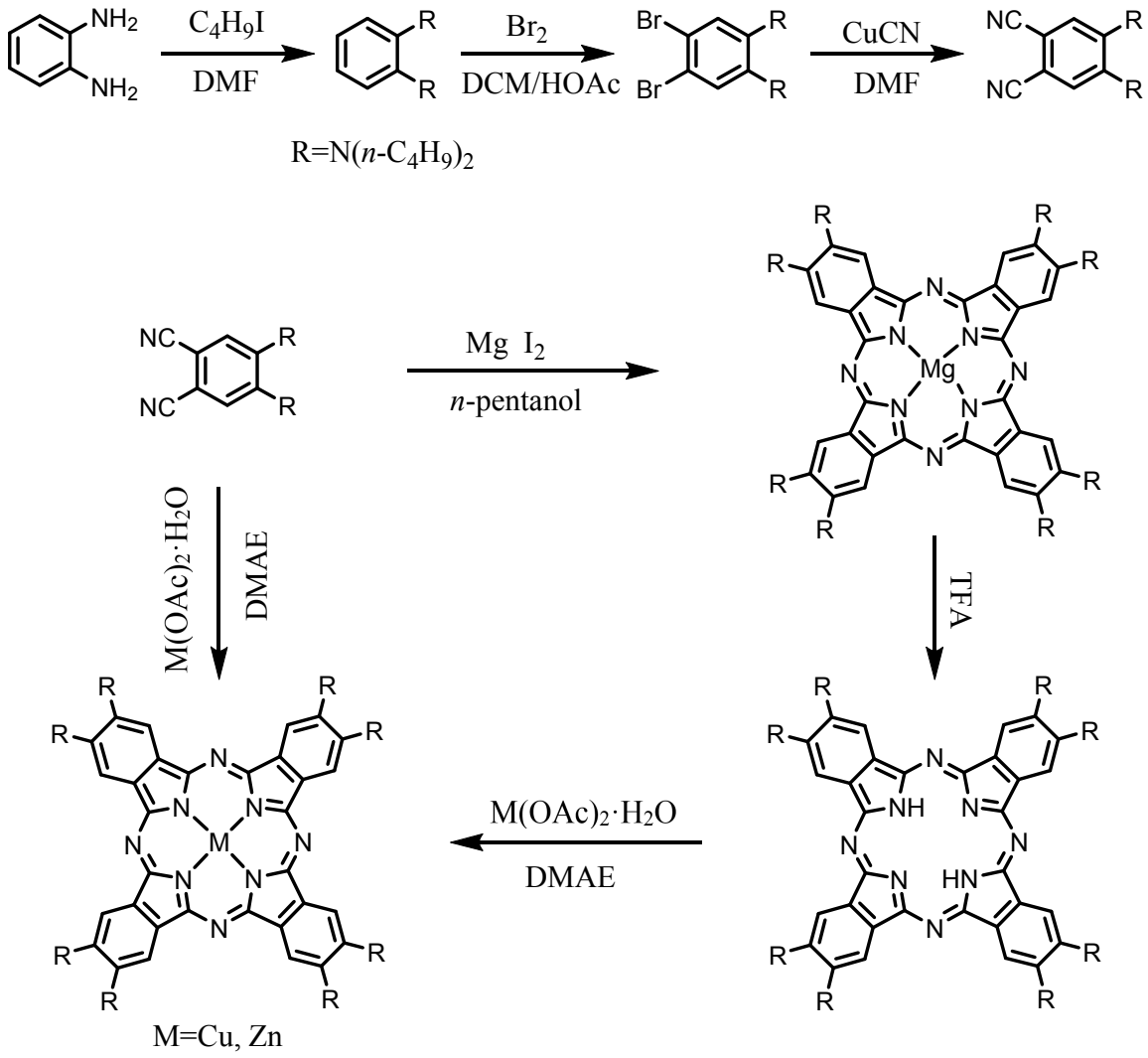
Table S1. Analytical and mass spectrometric data for **1-4**.

Table S2. ^{1}H NMR data (δ) for **1**, **2**, and **4** recorded with the concentration of *ca.* 1.0 × 10^{-3} M at 25°C.

Table S3. Crystal data and structure refinements for **1** and **4**.

Table S4. Selected bond lengths of **1**.

Table S5. Selected bond lengths of **4**.



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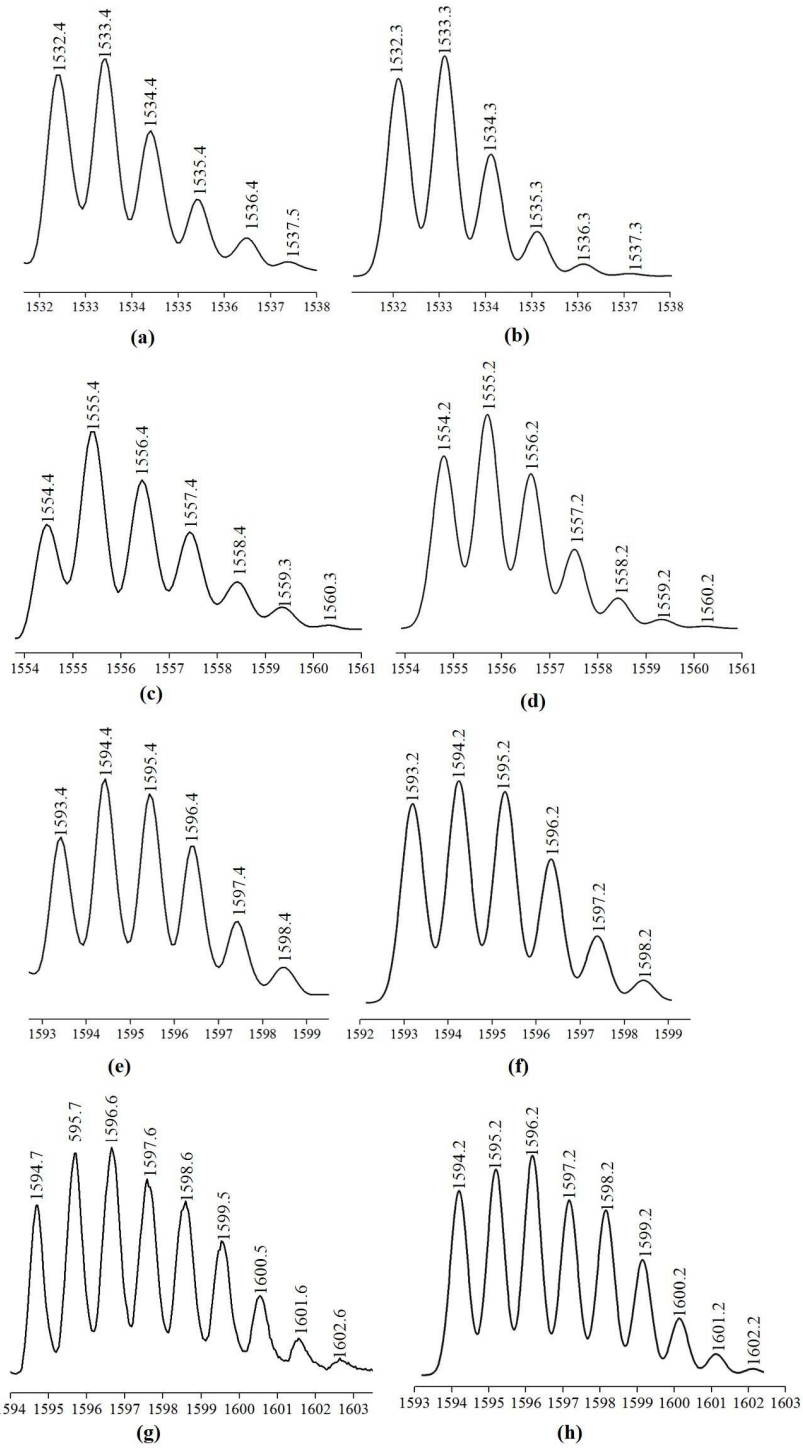


Figure S1. (a) Experimental and (b) simulated isotopic patterns for **1**; (c) Experimental and (d) simulated isotopic patterns for **2**; (e) Experimental and (f) simulated isotopic patterns for **3**; (g) Experimental and (h) simulated isotopic patterns for **4**.

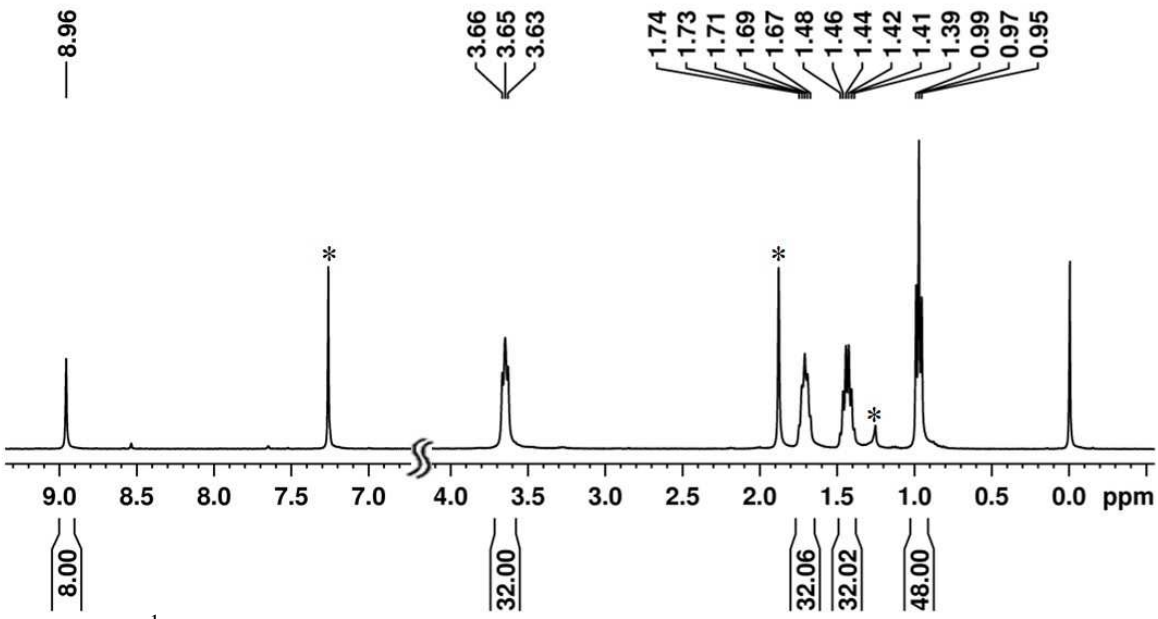


Figure S2. ^{1}H NMR spectrum of **2** recorded in $CDCl_3$/[D_5]pyridine (v/v = 150:1) at 25°C. The signals due to the residue $CHCl_3$, H_2O, and petroleum ether are denoted as *.

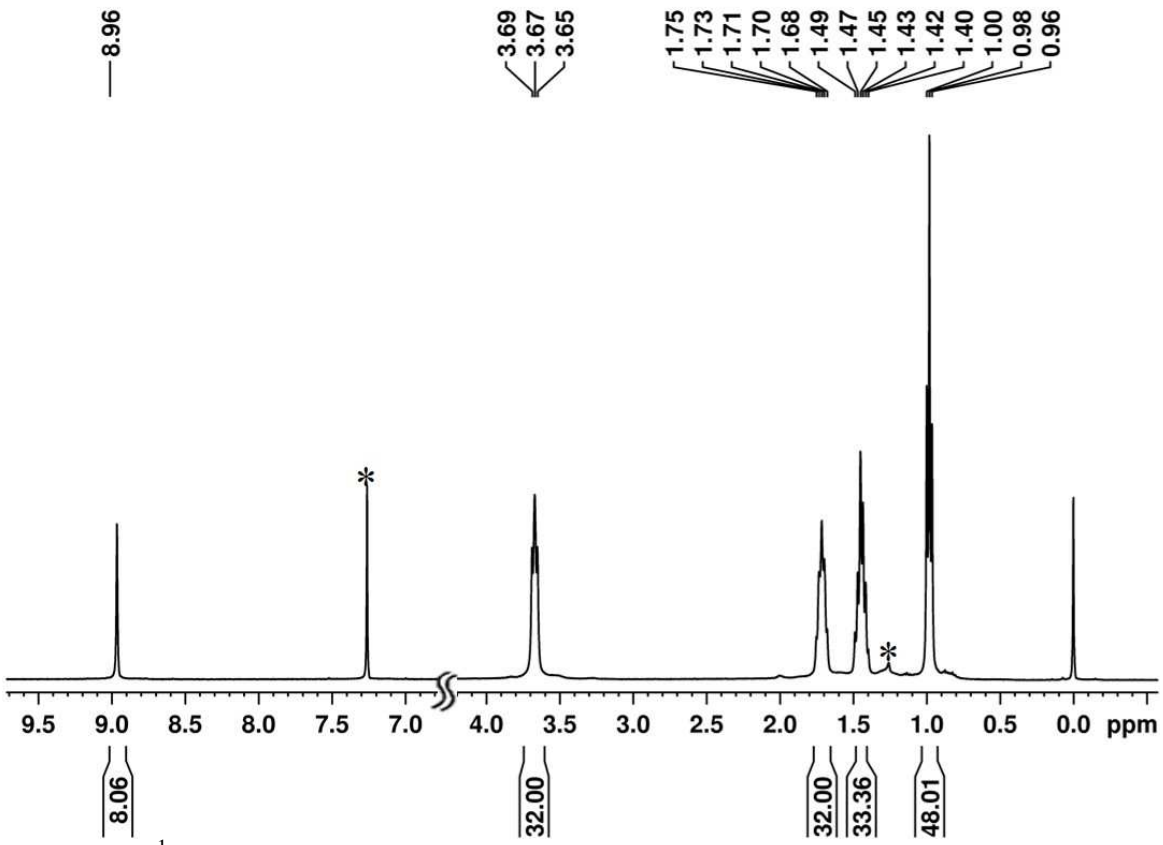
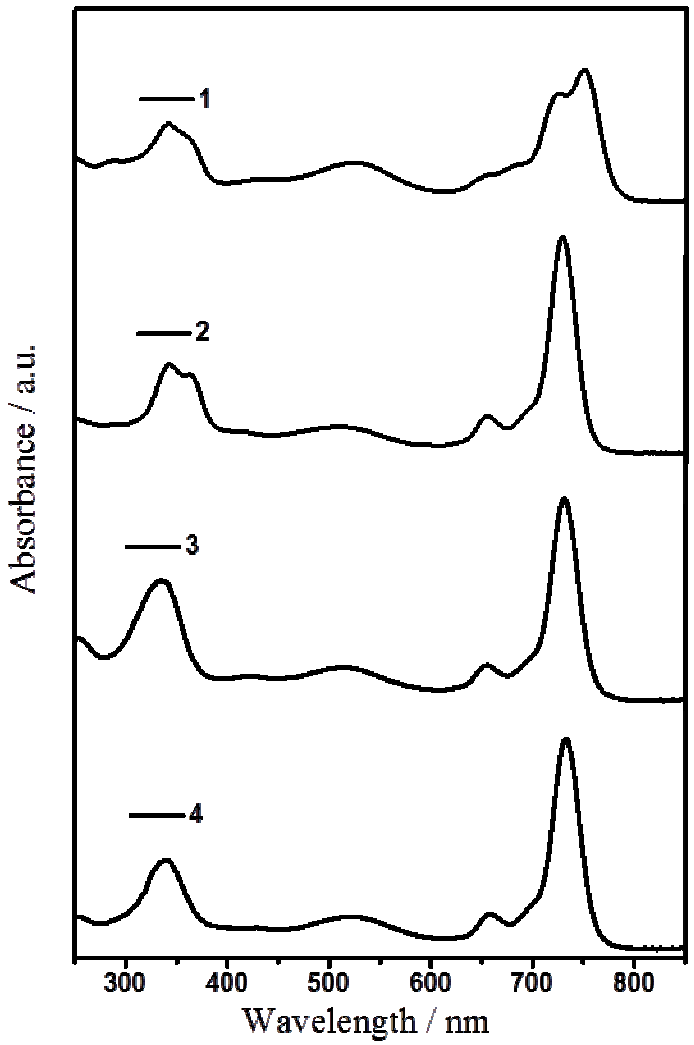


Figure S3. ^{1}H NMR spectrum of **4** recorded in $CDCl_3$ at 25°C. The signals due to the residue $CHCl_3$ and petroleum ether are denoted as *.



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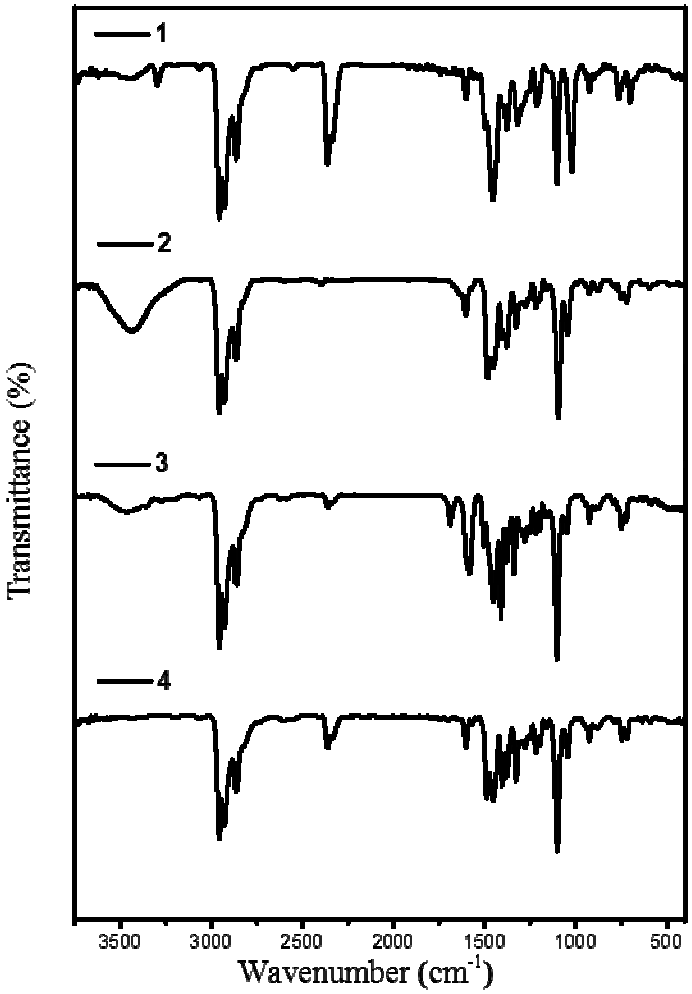

Figure S5. IR spectra of M{Pc[N(C_4H_9)$_2$]$_8$} (M = 2H, Mg, Cu, Zn) (**1**-**4**).

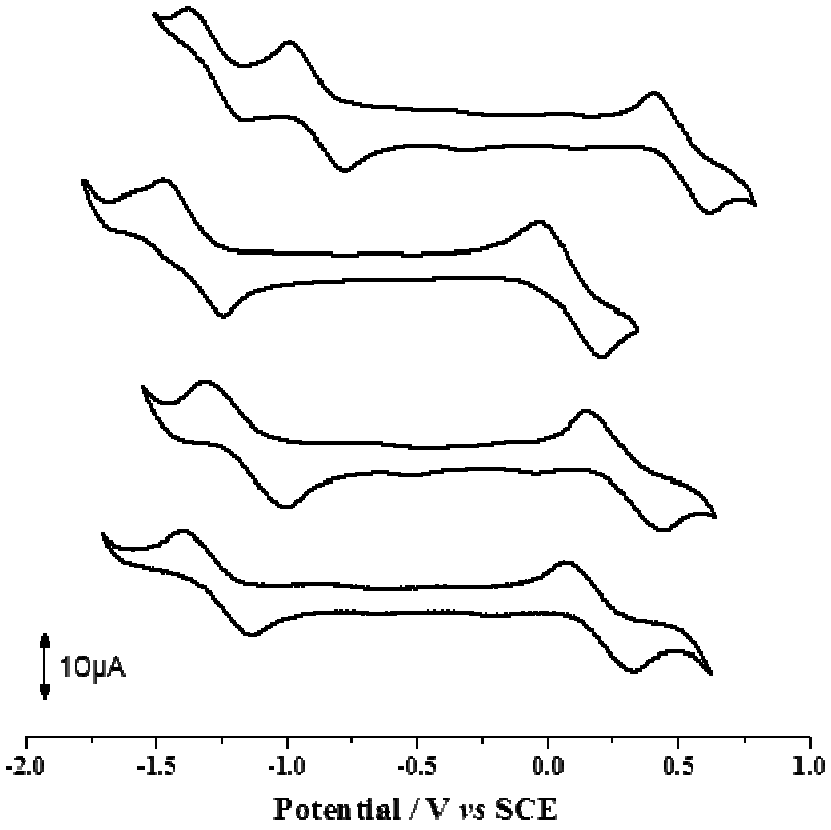

Figure S6. Cyclic voltammograms of **1**-**4** (from top to bottom) in CH_2Cl_2/pyridine (50:1) containing 0.1 mol dm^{-3} $[Bu_4N][ClO_4]$ at a scan rate of 30 mV s^{-1}.

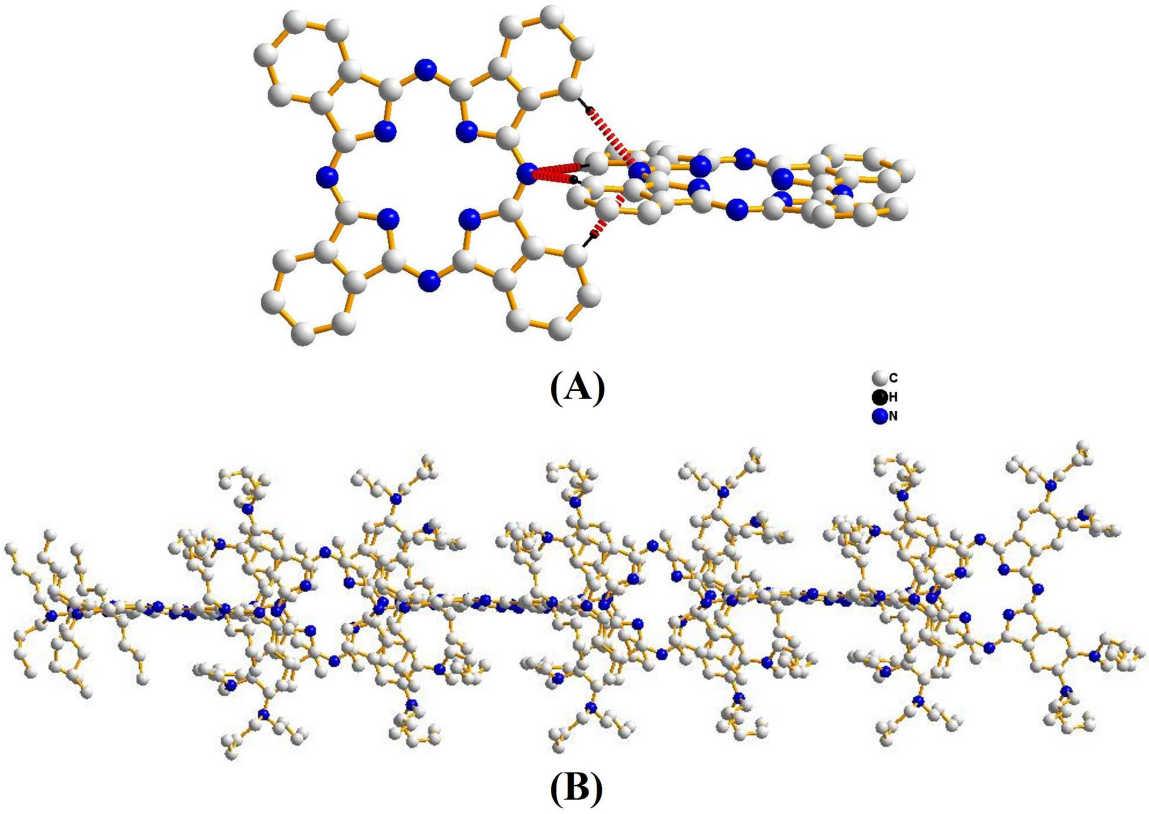

Figure S7. (A) Two adjacent $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) molecules connected depending mainly on the C-H···N hydrogen bonds formed between two C-H(α) bonds of one phthalocyanine and the meso-N atom of the another phthalocyanine with all the di-butylamino groups omitted for clarity. (B) 1-D supramolecular structure of **1** with all hydrogen atoms omitted for clarity.

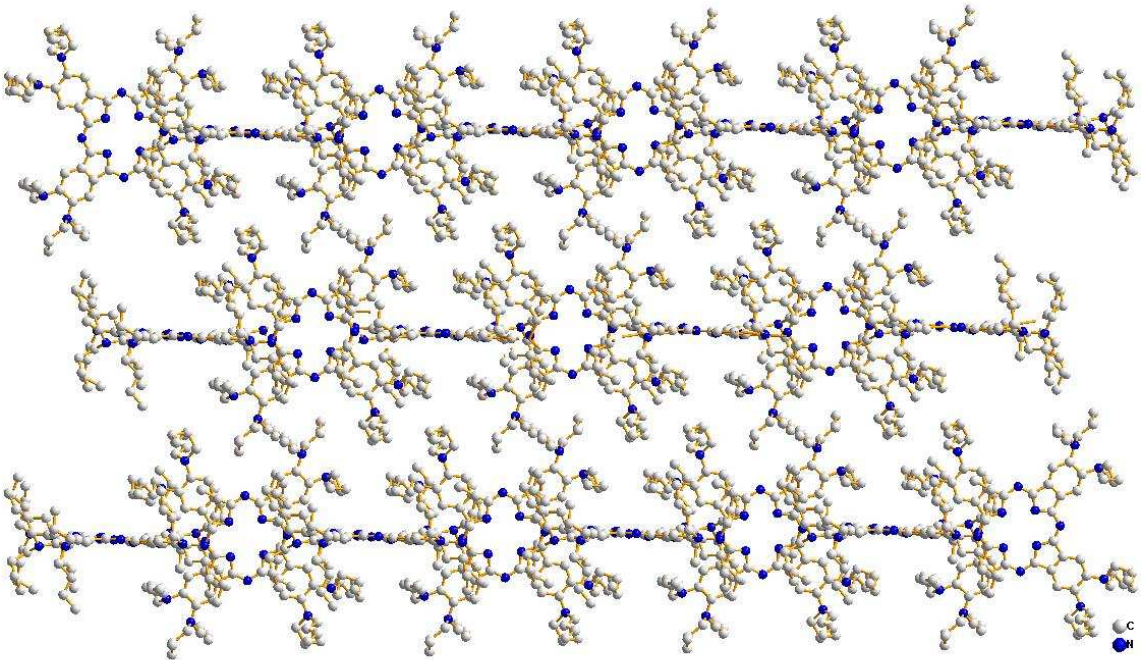

Figure S8. The three dimensional structure of $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) with all hydrogen atoms omitted for clarity.

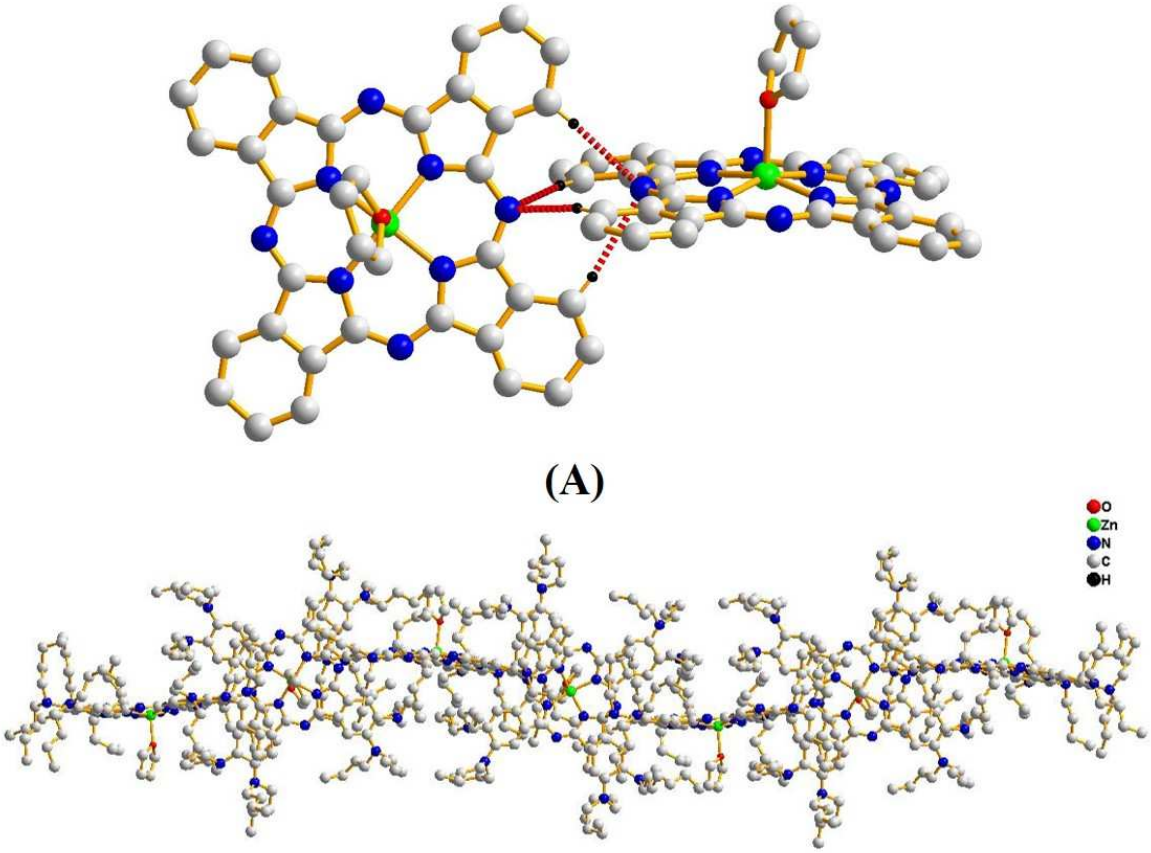

Figure S9. (A) Two adjacent Zn{Pc[N(C_4H_9)$_2$]$_8$} (**4**) molecules connected depending mainly on the C-H···N hydrogen bonds formed between two C-H(α) bonds of one phthalocyanine and the meso-N atom of the another phthalocyanine with all the di-butylamino groups omitted for clarity. (B) 1-D supramolecular structure of **4** with all hydrogen atoms omitted for clarity.

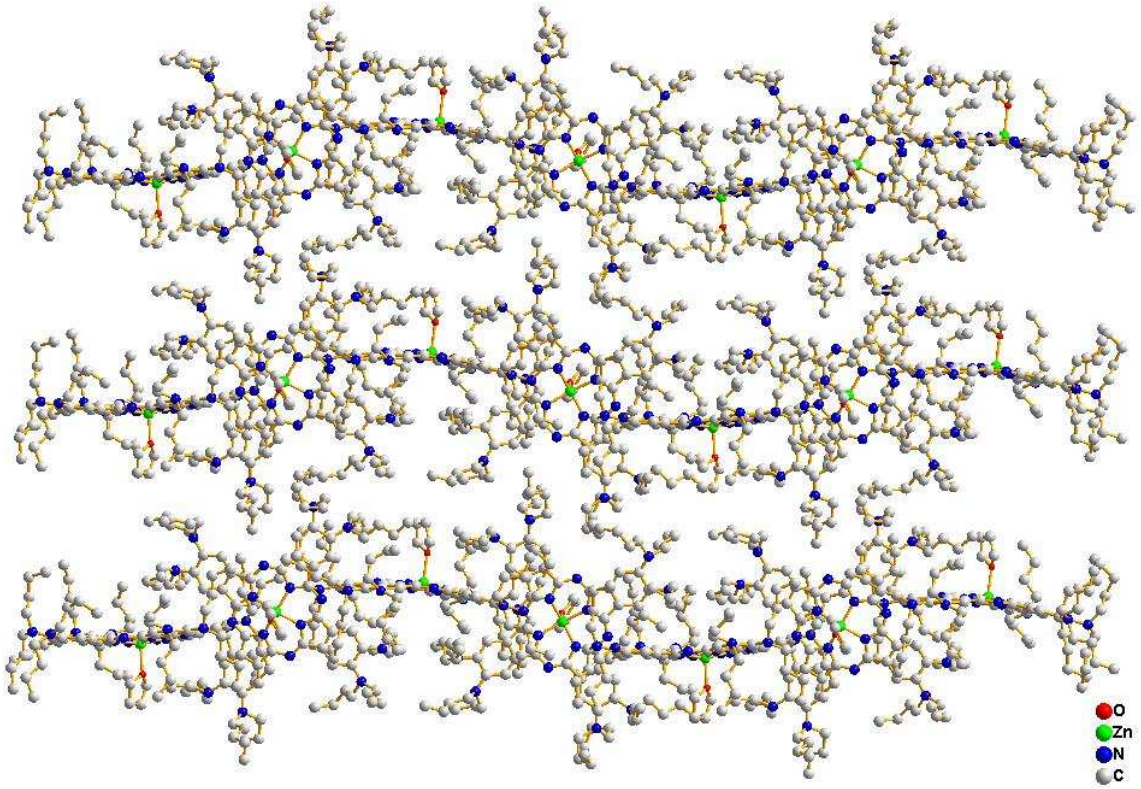

Figure S10. The three dimensional structure of $Zn\{Pc[N(C_4H_9)_2]_8\}$ (**4**) with all hydrogen atoms omitted for clarity.

Table S1. Analytical and mass spectrometric data for **1-4**.[a]

compound	$[M+H]^+$(m/z)	Analysis		
		C	H	N
1	1533.4 (1533.3)[b]	74.38 (74.42)[c]	9.90 (10.05)[c]	14.50 (14.41)[c]
2	1555.4 (1555.2)[b]	72.29 (72.25)[d]	9.95 (9.95)[d]	13.89 (13.82)[d]
3	1594.4 (1594.2)[b]	71.79 (71.79)[e]	9.59 (9.64)[e]	13.78 (13.88)[e]
4	1596.6 (1596.2)[b]	71.52 (71.51)[f]	9.87 (9.64)[f]	13.95 (13.83)[f]

[a] Calculated values given in parentheses. [b] By MALDI-TOF mass spectrometry. [c] Contain 0.125 equiv. solvated $CHCl_3$ and 0.25 equiv. solvated CH_3OH. [d] Contain 1.0 equiv. solvated H_2O and 1.5 equiv. solvated CH_3OH. [e] Contain 0.25 equiv. solvated H_2O and 0.5 equiv. solvated CH_3OH. [f] Contain 0.5 equiv. solvated H_2O and 0.5 equiv. solvated CH_3OH.

Table S2. ^{1}H NMR data (δ) for **1**, **2**, and **4** recorded with the concentration of *ca.* 1.0×10^{-3} M at 25°C.

	NH	α-Pc	*n*-Bu			
			CH_2	CH_2	CH_2	CH_3
1	0.20 (s, 2 H)	8.94 (s, 8 H)	3.66 (t, J = 6.96 Hz, 32 H)	1.71 (m, J = 7.30 Hz, 32 H)	1.44 (m, J = 7.23 Hz, 32 H)	0.98 (t, J = 7.28 Hz, 48 H)
2[a]	——	8.96 (s, 8 H)	3.65 (t, J = 7.38 Hz, 32 H)	1.70 (m, J = 7.29 Hz, 32 H)	1.42 (m, J = 7.32 Hz, 32 H)	0.96 (t, J = 7.32 Hz, 48 H)
4	——	8.96 (s, 8 H)	3.67 (t, J = 7.38 Hz, 32 H)	1.71 (m, J = 7.34 Hz, 32 H)	1.44 (m, J = 7.31 Hz, 32 H)	0.98 (t, J = 7.32 Hz, 48 H)

[a] recorded in $CDCl_3$/[D_5]pyridine (150:1).

Table S3. Crystal data and structure refinements for **1** and **4**.

Compound	**1**	**4**
formula	$C_{96}H_{154}N_{16}$	$C_{100}H_{160}N_{16}OZn$
fw	1532.35	1667.81
crystal system	monoclinic	orthorhombic
space group	*C*2/c	$C222_1$
a	20.0317(10)	16.7399(6)
b	27.6755(11)	28.7996(16)
c	18.5820(9)	40.3572(10)
α	90.00	90.00
β	116.117(6)	90.00
γ	90.00	90.00
V	9249.8(7)	19456.3(14)
Z	4	8
θ range (deg)	3.14-63.00	3.05-63.00
F_{calcd} (g/cm^3)	1.100	1.139
μ(mm^{-1})	0.497	0.759
F(000)	3368	7280
R_1 ($I>2\theta$)	0.0575	0.1137
R_{w2} ($I>2\theta$)	0.1426	0.3004
R_{w2} for all	0.1557	0.3215
GOF on F^2	1.046	1.256
CCDC number	1412942	1412943

Table S4. Selected bond lengths of **1**.

Bonds	**1**
C(18)-N(4)	1.424(3)
C(20)-N(5)	1.422(3)
C(23)-N(6)	1.418(3)
C(24)-N(7)	1.416(3)

Table S5. Selected bond lengths of **4**.

Bonds	**4**
N(1)-C(4)	1.44(3)
N(2)-C(5)	1.44(4)
N(3)-C(12)	1.40(3)
N(4)-C(13)	1.43(3)
N(5)-C(20)	1.43(2)
N(6)-C(21)	1.42(2)
N(7)-C(28)	1.435(18)
N(8)-C(29)	1.452(18)