Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.


# Electronic Supplementary Information

## ABAB-type Phthalocyanines Simultaneously Bearing Electron Donating and Electron Accepting Groups. Synthesis, Spectroscopy, and Structure

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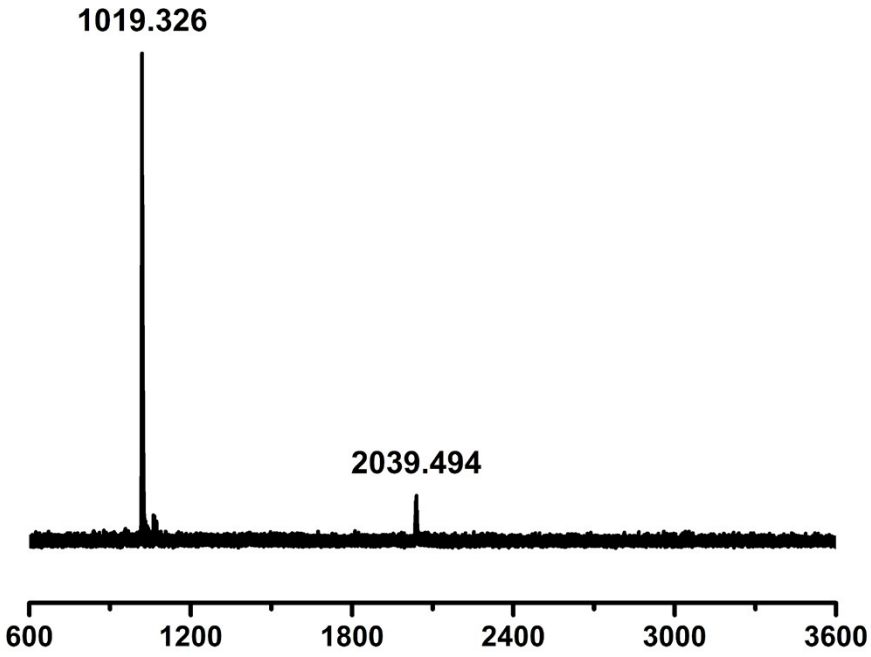


**Fig. S1**. MALDI-TOF mass spectra of **1**.

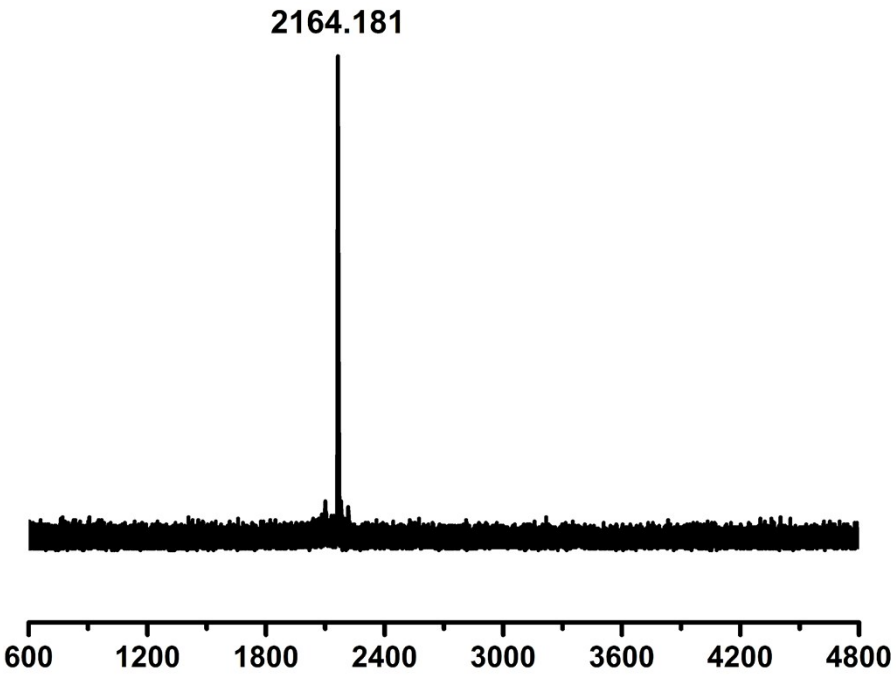


**Fig. S2**. MALDI-TOF mass spectra of **2**.

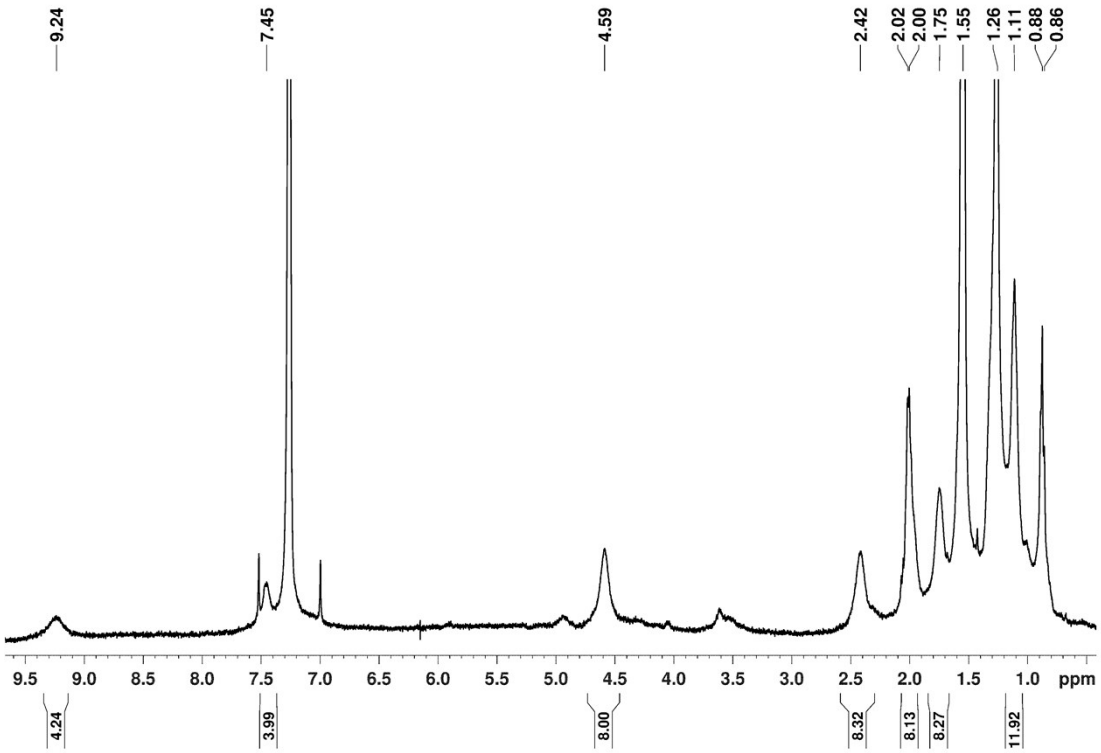


**Fig. S3**. $^{1}$H NMR spectrum of Mg(DADAPc) (**1**) recorded in $CDCl_3$ at room temperature.

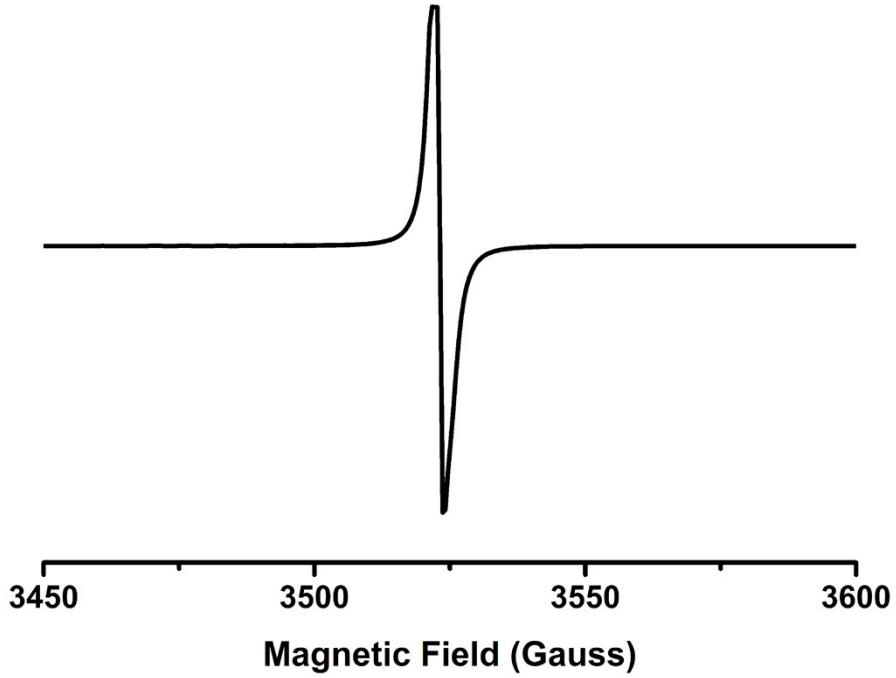


**Fig. S4**. Powder ESR spectrum of **2** at room temperature.

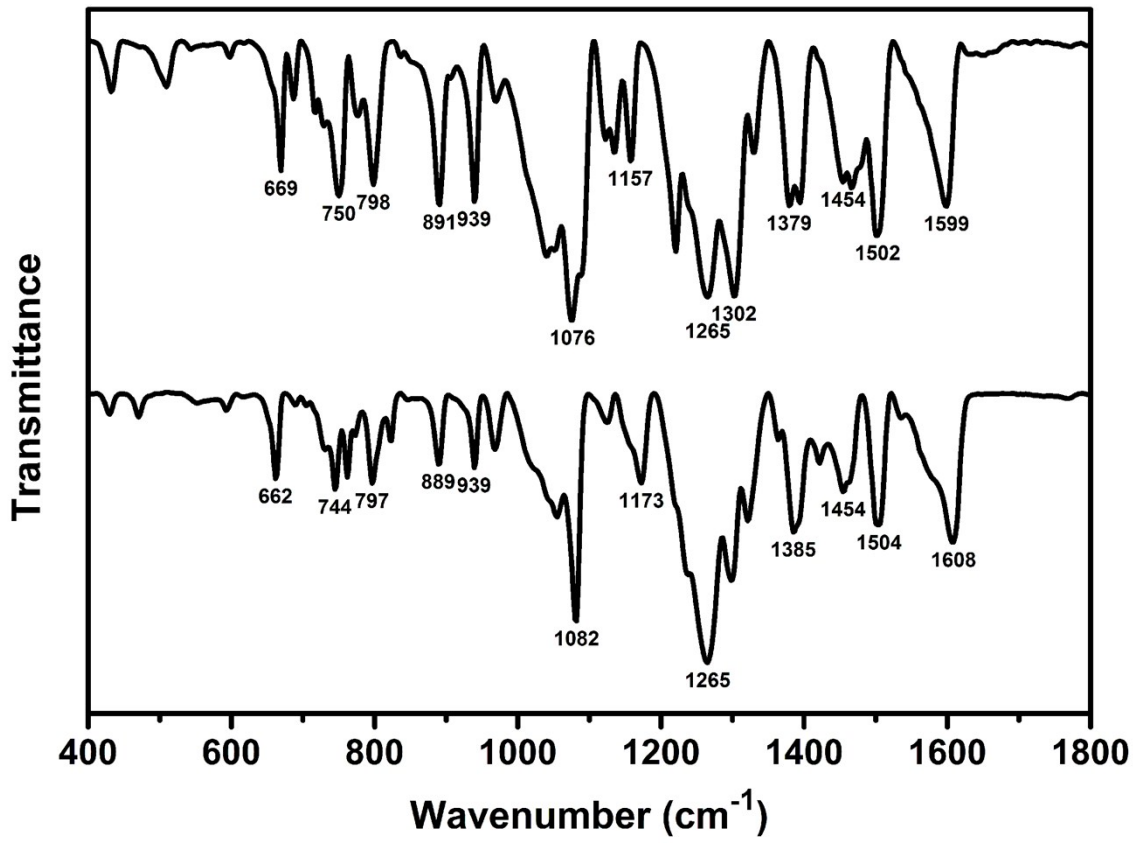


**Fig. S5**. IR spectra of **1** and **2** in the region of 400-1800 $cm^{-1}$ with 2 $cm^{-1}$ resolution.

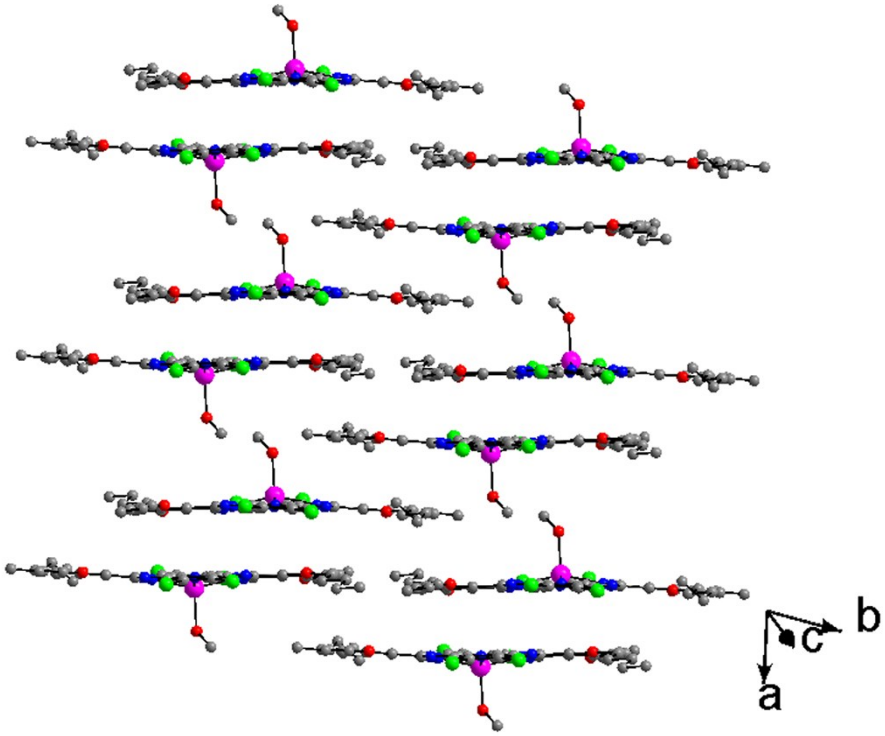


**Fig. S6.** Molecular packing in single crystals of **1** with hydrogen atoms omitted for clarity.

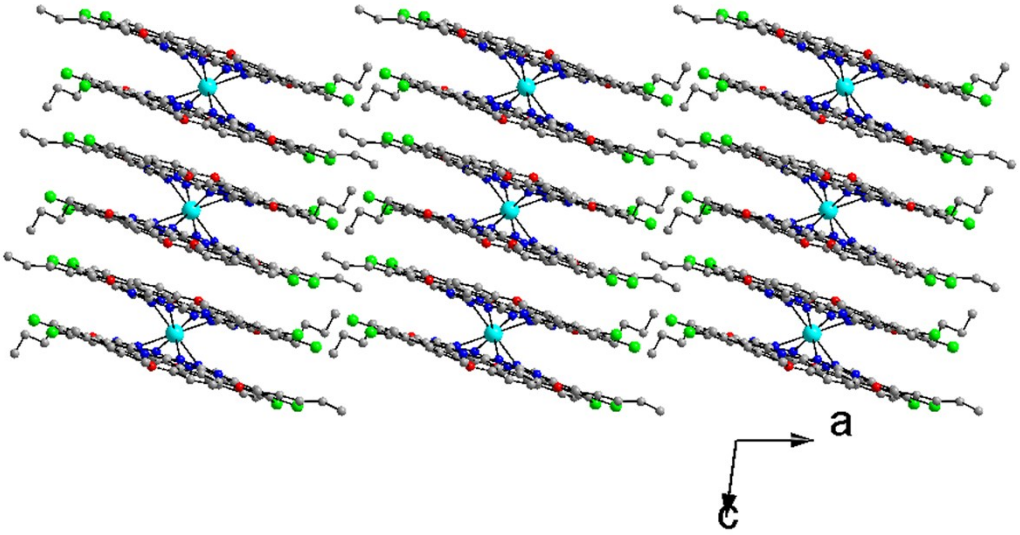


**Fig. S7**. Molecular packing in single crystals of **2** with hydrogen atoms omitted for clarity [Lu turquiose, C grey, N blue, O red and Cl green].

**Table 1.** Analytical and mass spectroscopic data for **1** and **2**.

| Compound | Yield (%) | $[M+H]^+$ (*m/z*)[a,b] | Analysis (%)[a] | | |
|---|---|---|---|---|---|
| | | | C | H | N |
| MgPc(ABAB) (**1**)[c] | 6.2 | 1019.3 (1019.3) | 60.29(60.56) | 5.18(5.37) | 10.81(10.66) |
| $Lu^{III}[Pc(ABAB)]_2$ (**2**) [d] | 58 | 2164.2 (2164.5) | 55.12(55.22) | 4.64(4.63) | 9.91(9.81) |

[a] Calculated values given in parentheses. [b] By MALDI-TOF mass spectrometry. The value corresponds to the most abundant isotopic peak of the protonated molecular ion $[M+H]^+$. [c] Contain 1 equiv. of solvated $CH_3OH$. [d] Contain 1 equiv. of solvated $CHCl_3$.

**Table S2.** Electronic absorption data for **1** and **2** in $CHCl_3$. ·

| Compound | $\lambda_{max}$/nm (log ε) | | |
|---|---|---|---|
| **1** | 348(4.75) | 658(4.48) | 726 (5.04) |
| **2** | 330(5.18) | 718(5.13) | 1725(4.20) |

**Table S3.** Structural data for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| average M-N(isoindole) bond distance [Å] | 2.036 | 2.376 |
| M-$N_4$(isoindole) plane distance [Å] | 0.456 | 1.337 |
| interplanar distance [Å] | 3.379[a] | 2.674 |
| average dihedral angle ϕ between $N_4$ mean plane and isoindole ring bearing the two pentyloxy chains [°] | 3.36 | 9.07 |
| average dihedral angle ϕ between $N_4$ mean plane and isoindole ring bearing the two chloride atoms [°] | 3.66 | 6.52 |
| average twist angle [°] [b] | ------ | 42.30 |
| the nearest M…M distance | 5.795 | 10.308 |

[a] Defined as the distance between two $N_4$ mean plane of one MgPc(ABAB) π dimer.

[b] Defined as the rotation angle of one macrocycle away from the eclipsed conformation of the two macrocycles.

**Table S4**. Crystallographic data for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Molecular formula | $C_{54}H_{60}N_8O_6Cl_4Mg$ | $C_{104}H_{104}N_{16}Cl_8Lu$ |
| $M$ | 1083.21 | 2164.60 |
| Crystal system | **Triclinic** | **Monoclinic** |
| Space group | *P*-1 | *C*2/c |
| $a$/Å | 11.3936(12) | 36.9471(4) |
| $b$/Å | 15.0984(10) | 18.5389(2) |
| $c$/Å | 16.4187(15) | 14.4165(2) |
| $\alpha$/° | 83.898(7) | 90 |
| $\beta$/° | 89.844(8) | 97.5320(10) |
| $\gamma$/° | 69.577(8) | 90 |
| $U$/Å$^3$ | 2630.1(4) | 9789.5(2) |
| $Z$ | 2 | 4 |
| F(000) | 1136 | 4444 |
| $D_c$/Mg m$^{-3}$ | 1.368 | 1.469 |
| $\mu$/mm$^{-1}$ | 2.637 | 4.476 |
| Data collection range/° | 3.14 to 62.50 | 3.97 to 68.00 |
| Reflections measured | 13042 | 18042 |
| Independent reflections | 8233 (Rint = 0.0207) | 8827 (Rint = 0.0317) |
| Parameters | 665 | 622 |
| $R_1$ [$I>2\sigma(I)$] | 0.0452 | 0.0334 |
| $wR_2$ [$I>2\sigma(I)$] | 0.1206 | 0.0878 |
| Goodness of fit | 1.051 | 1.033 |