Electronic Supplementary Material (ESI) for RSC Advances.

Electronic supplementary information for

Amine-Assisted Solubilization of Unsubstituted Zinc Phthalocyanine for Film Deposition Purposes

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Part 1. Sample Preparation

Unsubstituted ZnPc was prepared from phthalonitrile (1.0 g, 7.8 mmol), zinc acetate (0.35 g, 1.9 mmol), and *N*,*N*-dimethylacetamide (5 drops) by heating at 165° C during 1 h. The product was washed with acetic acid to obtain ca. 0.80 g of dark needle-shaped crystals with intense purple reflex. The crystals were dissolved in 96 % sulfuric acid to obtain a saturated solution, which was filtrated, poured into acetonitrile, and allowed to stand still during 1 h. A compact dull green precipitate of the ZnPc sulfate salt was collected on a glass filter, washed acid free with acetone, and dried at room temperature. Next, ZnPc was regenerated from the salt in two ways. Firstly, the salt was treated with a minimal amount of concentrated aqueous ammonia and then thoroughly washed with ammonia-saturated methanol. Secondly, the salt was treated only with ammonia-saturated methanol. Thus, two intermediate products composed of ZnPc and ammonia sulfate were obtained. Because ammonia sulfate could not be removed by methanol, these products were stirred in hot water during 1 h to obtain two pure ZnPc samples.

Outwardly these samples look like uniform free-floating powders, but using an optical microscope allows one to discern a distinct difference between them: the former sample consists of microscopic lamellas (~ 10 ?m in length), while the latter one is a nanoscale powder. Molar extinction coefficient of the powdery sample was determined as 222000 at 670 nm in DMF, being close to that of the sublimed commercial product from TCI Chemicals (225000; https://www.tcichemicals.com/eshop/ru/ru/commodity/Z0037/).

Both samples were characterized by X-ray scattering measurements. Structural data were collected on a Bruker D8 Advance apparatus using the Ni-filtered Cu-*K*α radiation (λ = 0.15418 nm) with incident angles (2Θ) varying from 2° to 40° and a step size of 0.02°. To keep the X-ray beam properly focused, the Bragg–Brentano parafocusing geometry was applied. The scattering intensity was measured by a scintillation counter with count time of 4 sec per step. The raw data are shown in **Figure S1**.

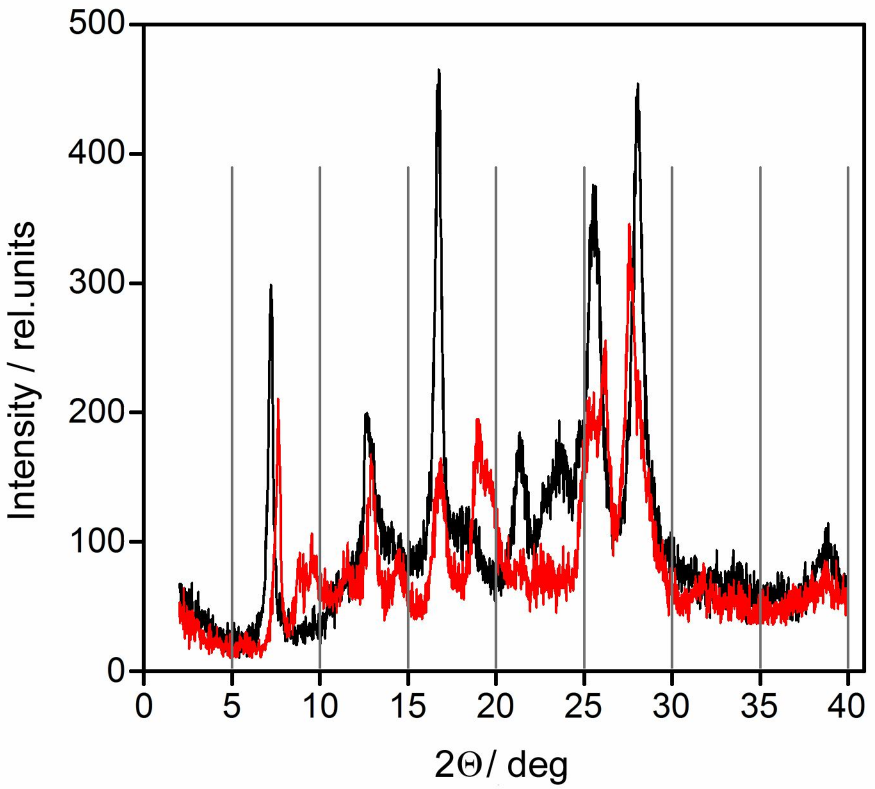

Figure S1. Uncorrected X-ray diffraction patterns of the lamellar (black) and powdery (red) samples of ZnPc regenerated from the dye sulfate salt by aqueous and methanolic ammonia, respectively.

Part 2. Dissolution and Deposition

Saturation concentrations of ZnPc (C_S) were measured as follows. Cylindrical vials with a powdery sample (ca. 50 mg) and a solvent (1.5–2.0 ml) were hand-shaken at room temperature during 5 min and then placed overnight into an air thermostat at (20±1 °C). A supernatant solution was accurately withdrawn from the vials and passed through a Spartan HPLC syringe filter (0.45 ?m). Then, aliquots of 150 ?l were taken by a 500 ?l Hamilton syringe. The aliquots were desolvated at 120 °C, solid residues were re-dissolved in 1500 ?l of pyridine, and obtained solutions were analyzed by spectrophotometry. The magnitude of molar extinction used in calculations was taken as 35000. All measurements were conducted in one and the same 0.1 cm cuvette. The measured C_S values are an average of four runs. Ammonia-saturated solvents were prepared by bubbling gaseous ammonia into liquids pre-cooled on an ice bath. Vials with a powdery sample and an ammonia-saturated solvent were tightly screwed up at ca. 15 °C, hand-shaken, and placed overnight into an air thermostat at (20±1 °C). The solubilizing effect of tertiary amines (**Figure S2**) was studied under the same conditions.

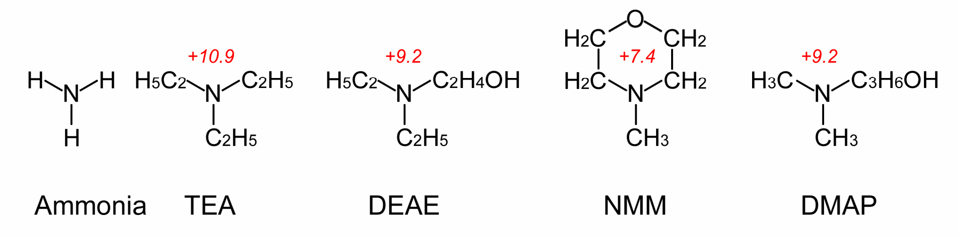

Figure S2. Amines for the dissolution experiment: TEA, triethylamine; DEAE, *N,N*-diethylaminoethanol; NMM, *N*-methylmorpholine; DMAP, *N,N*-dimethylaminopropanol. Italic decimals show acidity in water (pK_a).

Table S1. Saturation concentrations (C_S, mole per kg; 20 °C) of ZnPc in neat solvents.

No	Solvent	Abbr	Quality	C_S
1	Methanol	Met	*for HPLC*; LabScan, Poland	< 5e-7
2	Acetone	Ace	*puriss. spec*.; ChimMed, Russia	< 5e-7
3	Cyclopentanone	CyP	*p.a.*; Lvov Chemicals, Ukraine	< 5e-7
4	Chlorobenzene	ChB	99+ %; Sigma–Aldrich	< 5e-7
5	Triethylamine	TEA	99+ %; Sigma–Aldrich	(3.8 ± 0.2)e-5
6	Tetrahydrofuran	THF	*for HPLC*; ChimMed, Russia	(1.6 ± 0.3)e-4

Table S2. Saturation concentrations (C_S, mole per kg; 20 °C) of ZnPc in ammonia-saturated solvents.

No	Solvent	Ammonia, mole fraction †	C_S
1	Met	~ 0.3	< 5e-7
2	Ace	0.084	(2.4 ± 0.1)e-4
3	CyP	-	(2.1 ± 0.1)e-3
4	ChB	0.040	(2.4 ± 0.2)e-5
5	TEA	-	(2.1 ± 0.2)e-5
6	THF	-	(4.1 ± 0.4)e-4

† I. Short et al., Solubility of Ammonia and Hydrogen Sulfide... *J. Chem. Eng. Data* **1983**, *28*, 63; http://dx.doi.org/10.1021/je00031a019.

Table S3. Saturation concentrations (C_S, mole per kg; 20 °C) of ZnPc in the binary solvent–TEA systems (6:1, v/v).

No	Solvent	TEA, mole fraction	C_S
1	Met	0.070	< 5e-7
2	Ace	0.085	(7.7 ± 0.1)e-4
3	CyP	0.094	(4.6 ± 0.2)e-3
4	ChB	0.107	(6.0 ± 0.1)e-4

To test the binary solvent–amine systems on a subject of usability in thin film preparation, a number of systems composed of CyP (b.p. 131 °C) and tertiary aminoalcohols were saturated with ZnPc at room temperature. The obtained solutions were drop-cast onto an optical borosilicate glass pre-treated with 50 % hydrogen peroxide. The drops were dried at room temperature and the deposits were annealed.

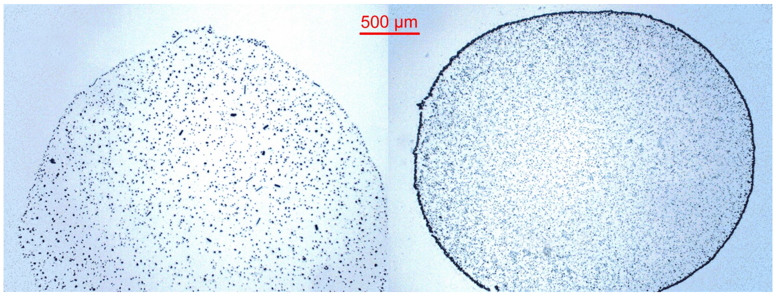

Figure S3. Patterns left from the ZnPc solutions in the CyP–DMAP (left) and CyP–DEAE (right) systems (6:1, v/v; non-annealed).

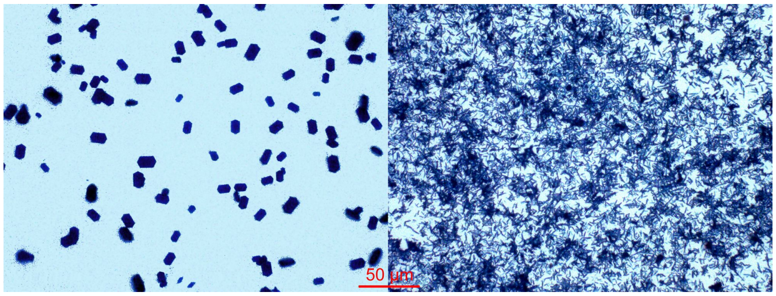

Figure S4. Patterns left from the ZnPc solutions in the CyP–DMAP (left) and CyP–DEAE (right) systems (6:1, v/v; annealed at 150 °C).

Note for **Figures S3** *and* **S4**

Herein, a key feature is a drastic difference in physicochemical effects exhibited by two structurally similar and equally volatile aminoalcohols (b.p. 163 °C for the both) on ZnPc crystallites. The patterns indicate that DEAE is a poorer eliminator of the coffee-ring effect than DMAP and of no use as a habit modifier.

Part 3. Soret Band Analysis

Deconvolution of the Soret band into Gaussian peaks (**Tables S4** and **S5**) was validated by two criterions. The correlation coefficient (r > 0.9995) was used as a general criterion. As a specific criterion, a good agreement of the deconvolution results (**Figure S5**) with the spectrum of ZnPc axially coordinated with the CN$^-$ anion at cryogenic temperature was used (see J. Mack et al., Band Deconvolution Analysis of the Absorption and Magnetic Circular Dichroism Spectral Data... *J. Phys. Chem*. **1995**, *99*, 7935; http://dx.doi.org/10.1021/j100020a015).

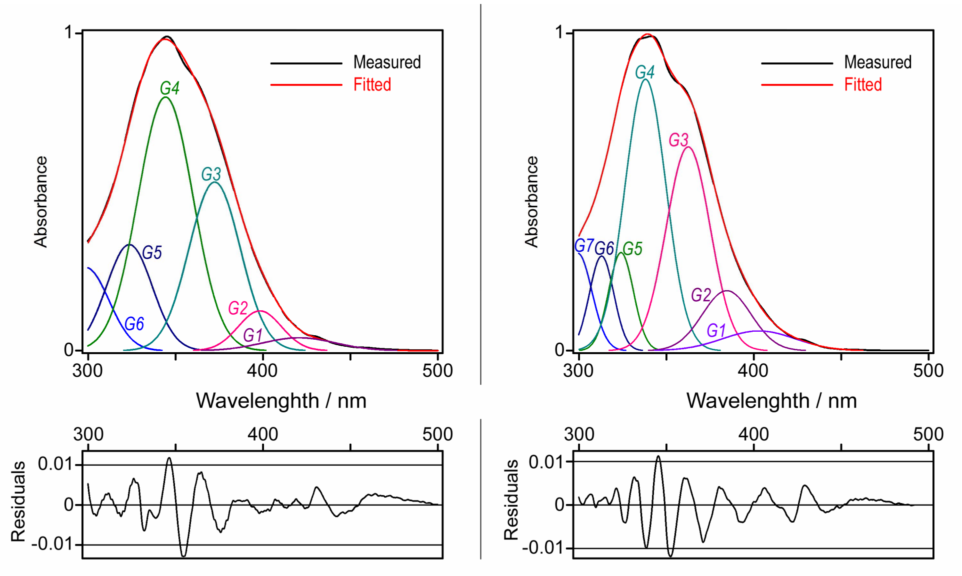

Figure S5. Gaussian deconvolution of the spectra of ZnPc in the binary CyP–TEA system (left) and neat TEA (right).

Table S4. Gaussian components of the Soret band in **Figure S5, left**.

Index	**Type**	**Parameter**				**λ from Table 3, in ref †**
		λ_0	**λ**	***A***	***S***	
-	2^{nd} $\pi \rightarrow \pi^*$	-	~ 430	~ 0.05	-	435
G1	B1	425	421	0.04	2.7	406
G2	B1	400	398	0.13	5.1	391
G3	B1	380	372	0.54	25.5	375
G4	B2	350	344	0.81	41.2	348
G5	B2	325	324	0.34	14.3	325
G6	B3	300	299	0.26	11.2	306

Abbr: λ_0 and λ, input and output centers, nm; *A*, height, rel. units; *S*, area, %.

† G. Ricciardi et al., Ground and Excited States of Zinc Phthalocyanine... *J. Phys. Chem. A* **2001**, *105*, 5242; http://dx.doi.org/10.1021/jp0042361.

Table S5. Gaussian components of the Soret band in **Figure S5, right**.

Index	**Type**	**Parameters**				**λ as in Table S4**
		λ_0	**λ**	***A***	***S***	
-	2^{nd} $\pi \rightarrow \pi^*$	-	~ 430	~0.05	-	435
G1	B1	425	402	0.06	4.4	406
G2	B1	400	385	0.19	9.1	391
G3	B1	375	363	0.65	28.1	375
G4	B2	345	338	0.86	35.0	348
G5	B2	330	324	0.31	7.6	325
G6	B2	320	313	0.30	7.2	-
G7	B3	300	300	0.31	8.6	306

Abbr as in **Table S4**.

Part 4. DFT Calculations

Molecular modelling was performed by the DFT method with the software package Gaussian09. All calculations were carried out by using the Becke3–Lee–Yang–Parr correlation functional with the 6-31G(d,p) basis set.

Optimized geometric parameters of the ZnPc molecule (**Figure S6**) are listed in **Table S6**. A lack of imaginary frequency modes for the optimized geometry proved that a found minimum on the potential energy surface was true.

The energies of interactions between ZnPc and small molecules (Met, Ace, and ammonia) were calculated as a difference between the total energy of a molecular complex and a sum of the total energies of ZnPc and individual small molecules. Full geometry optimization was performed for each distance value of the reaction coordinate in the ZnPc–molecule systems; that is, molecular geometries for the whole structures were optimized when a constraint in the interatomic distances (e.g., Zn–N) was kept. The obtained data are listed in **Table S7**.

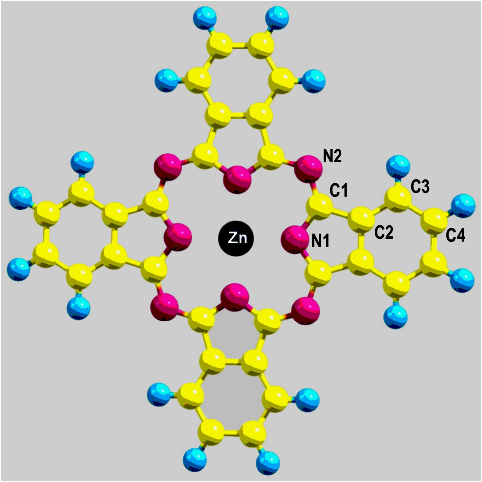

Figure S6. Molecular structure of ZnPc. Bond length and angles are listed in **Table S6**.

Table S6. Geometric parameters of the ZnPc molecule (**Figure S6**).

Bond length and angles	**DFT calculations** *			**Structural experiment** *	
	A	***B***	***C***	***D***	***E***
Zn-N1	1.990	1.992	2.002	1.980	1.954
N1-C1	1.373	1.373	1.387	1.369	1.374
C1-N2	1.330	1.330	1.335	1.331	-
C1-C2	1.460	1.461	1.461	1.455	1.420
C2-C3	1.395	1.395	1.396	1.393	1.370
C3-C4	1.394	1.395	1.399	1.391	1.369
C2-C2	1.410	1.410	1.417	1.400	1.550
C4-C4	1.407	1.408	1.411	1.396	1.383
C3-H	1.085	-	1.084	-	-
C4-H	1.086	-	1.085	-	-
Zn-N1-C1	125.3	-	125.4	-	-
N1-C1-N2	127.5	-	127.0	-	-
C1-N2-C1	124.4	124.4	-	123.5	125.6
C1-N1-C1	109.4	109.5	109.1	109.1	106.9
C2-C1-N1	108.8	108.7	108.7	108.8	113.0
C2-C2-C1	106.5	106.5	106.8	106.6	103.5
C2-C2-C3	121.1	-	121.0	-	-
C2-C3-C4	117.8	117.8	117.9	117.3	121.6
C3-C4-C4	121.2	121.2	121.1	121.5	-

* ***A***, DFT-B3LYP/6-31G(d,p), ours; ***B***, DFT-B3LYP/6-31G(d), ref †; ***C***, DFT-B3LYP/6-31G, ref ‡; ***D***, X-ray diffraction, ref †; ***E***, electron diffraction in the gaseous phase, ref †.

† L. T. Ueno et al., Theoretical Studies of Zinc Phthalocyanine Monomer... *J. Mol. Struct. (Theochem)* **2009**, *899*, 71; https://doi.org/10.1016/j.theochem.2008.12.013.

‡ G. S. S. Saini et al., Zinc Phthalocyanine Thin Film and Chemical Analyte Interaction... *J. Phys. (Condens. Matter)* **2009**, *21*, 225006; https://doi.org/10.1088/0953-8984/21/22/225006.

Table S7. Calculated interaction energies in the ZnPc–molecule complexes.

Molecular entity	**Total energy, eA^{-3}**	**Interaction energy, kJ·mole^{-1} †**	
		A	***B***
Molecules			
ZnPc	-3446.39206269	-	-
Met	-115.723963037	-	-
Ace	-193.164213332	-	-
NH_3	-56.5577682613	-	-
Complexes			
ZnPc·Ace	-3639.56133485	-13.3	-
ZnPc·Met	-3562.13218539	-42.5	-51.1
ZnPc·NH_3	-3502.979855	-78.3	-84.9
ZnPc·2NH_3	-3559.539762	-84.5	-

† ***A***, DFT-B3LYP/6-31G(d,p), ours; ***B***, DFT-B3LYP/6-31G(d), ref ‡.

‡ G. S. S. Saini et al., Zinc Phthalocyanine Thin Film and Chemical Analyte Interaction... *J. Phys. (Condens. Matter)* **2009**, *21*, 225006; https://doi.org/10.1088/0953-8984/21/22/225006.

Part 5. MEP Maps

Three-dimensional maps of the molecular electrostatic potential (MEP) were generated by the software package GaussView 5.0. When launched, this program surveys all of the potentials on the map and finds the most negative and most positive potentials. Such regions are colored red and dark blue, respectively. So, red areas are characterized by an abundance of electrons; blue areas are characterized by a deficiency of electrons. Then, intermediate potentials are assigned colors according to the standard color spectrum: red (most negative), yellow, green, light blue, dark blue (most positive). When the program is allowed to select colors automatically, it uses a *default color scale* to equate different potentials with different colors. The surface onto which the potential is mapped can be calculated at different electron density levels, thus displaying the regions, where the electron density is larger than some cut-off value, as a three-dimensional surface.

Herein, the initial **map I** (**Figure S7**) of the ZnPc molecule was generated by using the DFT data from **Table S6** (**column *A***). The related cutoff density value of 0.0004 eA^{-1} was set by default. Then, the cutoff density value was changed forcedly step-by-step to generate a series of maps with MEP surfaces located closer to the polyatomic skeleton of the macroheterocycle (**Figure S7, maps II–V**). MEP values on three kinds of particular molecular fragments (**Table S8**) were expressed in relative units and used to substantiate the initial map as the best basis for analysis of the electron density in the molecular complexes.

Maps of the complexes are shown in **Figure S8**.

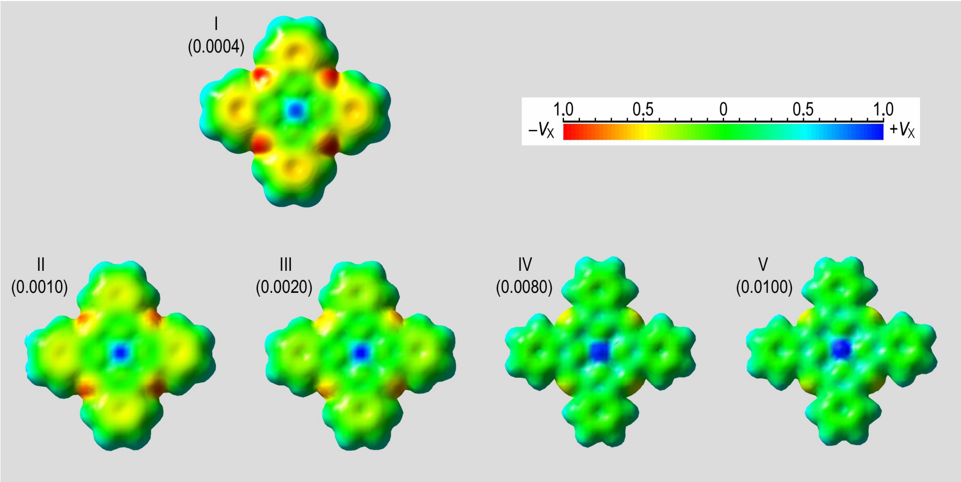

Figure S7. Three-dimensional MEP maps of the free ZnPc molecule at various cutoff densities (eA^{-1}, in parenthesis). The extreme MEP values ($\pm V_X$, eA^{-3}) are listed in **Table S8**.

Table S8. Molecular electrostatic potential (MEP, eA^{-3}) for the ZnPc molecule in **Figure S7**.

Map	**Isodensity surface (eA^{-1})**	**Extreme MEP, ($\pm V_X$, eA^{-3})**	**MEP on three kinds of particular molecular fragments (% of V_X)**		
			***meso*-Nitrogen atoms**	**Benzene rings**	**Macroheterocycle**
I	0.0004	0.02898	-98%	-52%	-16%
II	0.001	0.04248	-78%	-42%	-10%
III	0.002	0.06320	-50%	-32%	-6%
IV	0.008	0.133	-48%	+4%	+6%
V	0.01	0.152	-48%	+4%	+6%

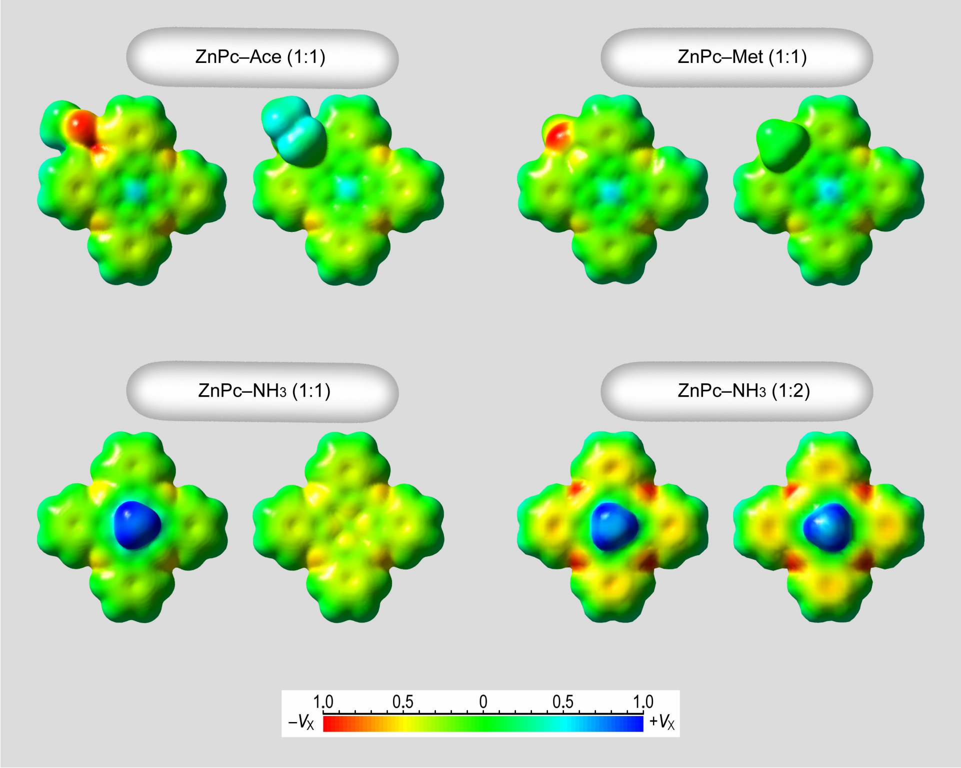

Figure S8. Three-dimensional MEP maps of the molecular complexes at the cutoff density value of 0.0004 eA^{-1}. The extreme MEP values ($\pm V_X$, eA^{-3}) are 0.04941 (ZnPc–Ace), 0.05146 (ZnPc–Met), 0.05870 (ZnPc–NH_3), and 0.03501 (ZnPc–$2NH_3$).