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Graphical Abstract



A3B type unsymmetrical and amphiphilic phthalocyanines: Synthesis, characterization, thermal stability and aggregation studies

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This study reports the preparation, analysis, aggregation statuses and thermal properties of five phthalocyanines. The preparation of all molecules includes two steps: the first step is the preparation of phthalocyanine precursor molecules (**A** and **B** coded phthalonitriles); the second step is the synthesis of one metal-free and four metalled phthalocyanines (**A**₃**B**-**Co**, **A**₃**B**-**Cu**, **A**₃**B**-**H**, **A**₃**B**-**Ni**, and **A**₃**B**-**Zn** coded compounds). Compound **A** holds a hydrophobic chain (cetyl alcohol); compound **B** holds a hydrophilic chain (tetraethylene glycol). Phthalocyanines include three hydrophobic chains and one hydrophilic chain (A₃B type phthalocyanine). Characterization methods which were used to determine the structure of these compounds are Fourier Transform Infrared (FTIR), Proton Nuclear Magnetic Resonance (¹H NMR), Carbon-13 Nuclear Magnetic Resonance (¹³C NMR), and Ultraviolet Visible (UV Vis) spectroscopies and elemental analysis. The phthalocyanines have high stability up to 260 °C as a minimum value. Aggregation statuses of the phthalocyanines change to the metal from the metal or to the solvent from the solvent.

Keywords: Phthalocyanine aggregation; Phthalocyanine; Thermal analysis; Amphiphilic phthalocyanines; Phthalocyanine synthesis; Unsymmetrical synthesis of phthalocyanines.

1. Introduction

Phthalocyanines (Pcs) were discovered for the first time by Braun and Tcherniac in 1907 [1]. The compounds have advantageous properties such as tinctorial characteristic, high stability, moderately cost of production, absorption in visible spectrum [2], inclusion capability of the different metals. Due to their outstanding properties, they have a wide range of applications areas in various fields such as laser recording materials, information storage systems, electrochromic display devices [3], chemical sensors [4], liquid crystals [5], catalysis [6], non-linear optics [7], Photodynamic Therapy (PDT) [8], nanotechnology [9], semiconductor devices [10], dye-sensitized solar cells [11], Langmuir-Blodgett films [12].

The synthesis of the symmetric metal-free and metalled phthalocyanines is well known, on the other hand, unsymmetrical synthesis of the phthalocyanines attracted attention in the recent years. Some studies in this field were listed in [13-22]. The unsymmetrical phthalocyanines have unique electronic and optical properties, and different synthesis strategies. Their synthesis and purification is more difficult from the others [2]. It has been reported a few methods in the literature for the synthesis of A₃B type unsymmetrical phthalocyanines such as statistical condensation method [23], polymerization strategy [24, 25], Ring-Opening Metathesis Polymerization (ROMP)-capture-release [26], ring expansion of subphthalocyanines [27-29].

In this study, our aim is to synthesize new A₃B type unsymmetrical metal-free and metallo phthalocyanines, to characterize their structures, to determine their aggregation tendency in some organic solvents and thermal stabilities. We used statistical condensation method on the synthesis of the phthalocyanine and reported the results of these studies in the related sections. In this context, we chose and prepared two phthalonitrile derivatives which have the opposite characteristics from each other. One of the substituents in the derivatives is tetraethylene glycol (TEG), which is a member of polyethylene glycol (PEG) polymers. PEGs comprise of ethylene oxide units, O(CH₂)₂, and play an important role in drug delivery systems [30] because of their solubility both in water and organic solvents [31], selective tumour accumulation, protection against enzymatic degradation [32], prolonged circulation time in the body [33], less antigenicity and immunogenicity and more excellent tolerability [34].

2. Experimental

The equipment and material knowledge which were used in this study were provided in the supplementary information. Compound A [35] and compound B [36] was synthesized according to given literatures. 4-Nitro phthalonitrile was prepared as given in [37].

2.1. Synthesis

General synthesis procedure of the phthalocyanines: (A₃B-Co, A₃B-Cu, A₃B-H, A₃B-Ni,

A₃B-Zn; iii in Scheme 1)

A mixed solution of **A** (0.2 g, 0.54 mmol) and **B** (0.058 g, 0.18 mmol) was prepared in pentanol. The temperature of the solution was increased up to 90 °C and the solution was stirred at the same temperature for 30 minutes. Metal salt [except for **A₃B-H**, cobalt(II) chloride, CoCl₂, (0.046 g, 0.36 mmol); copper(II) chloride, CuCl₂, (0.048 g, 0.36 mmol); nickel(II) chloride, NiCl₂, (0.046 g, 0.36 mmol); zinc(II) acetate, Zn(OAc)₂, (0.066 g, 0.36 mmol)] and 1,8-Diazabicyclo(5.4.0)undec-7-ene, DBU, (0.3 mL, 2 mmol) were added to the mixture. The reaction mixture which was monitored by Thin Layer Chromatography (TLC) was heated at reflux under nitrogen atmosphere for 48 hours. All volatile organic compounds were removed by rotary evaporation. The colored solid was dissolved in chloroform (15 mL) and washed with water (15 mL) three times. The organic layer was dried with sodium sulfate (Na₂SO₄). The solvent was evaporated. All phthalocyanines were purified and separated with column chromatography (dichloromethane/methanol 100:0, 99:1, 98:2, 97:3, respectively). The same eluates were combined and concentrated to dryness.

A₃B type unsymmetrical cobalt phthalocyanine (A₃B-Co): Yield: 17% (0.046 g), FTIR (Attenuated Total Reflectance, ATR), v/cm⁻¹: 3100-3600 (-OH), 3071 (Ar. C-H), 2921, 2852 (Al. C-H), 1598, 1487, 1463 (C=C, C=N), 1281, 1235, 1124, 1094 (C-O-C), 826, 720. Elemental analysis: calcd (%) for C₉₂H₁₄₄N₈O₈Co: C 71.33; H 9.37; N 7.23. Found: C 71.29; H 9.34; N 7.19. UV Vis (CH₂Cl₂), λ_{max} nm (logε): 675 (5.24), 615 (4.83), 357 (5.00).

A₃B type unsymmetrical copper phthalocyanine (A₃B-Cu): Yield: 13% (0.036 g), FTIR (ATR), v/cm⁻¹: 3197 (-OH), 3068 (Ar. C-H), 2919, 2851 (Al. C-H), 1607, 1488, 1467 (C=C, C=N), 1231, 1116, 1093, 1052 (C-O-C), 824, 746, 719. Elemental analysis: calcd (%) for C₉₂H₁₄₄N₈O₈Cu: C 71.12; H 9.34; N 7.21. Found: C 71.08; H 9.30; N 7.18. UV Vis (CH₂Cl₂), λ_{max} nm (logɛ): 6678 (4.97), 623 (4.63), 387 (4.41), 335 (4.77).

A₃B type unsymmetrical metal-free phthalocyanine (A₃B-H): Yield: 8% (0.021 g), FTIR (ATR), v/cm⁻¹:3100-3600 (-OH), 3328 (-NH), 3065 (Ar. C-H), 2917, 2850 (Al. C-H), 1608, 1486, 1466 (C=C, C=N), 1240, 1119, 1094, 1058 (C-O-C) 821, 746, 721. ¹H NMR (400 MHz, CDCl₃) (δ: ppm): 8.36-6.97 (m, 12H Ar-H), 4.48-4.03 (m, 22H, O-CH₂-CH₂-O, O-CH₂-CH₂), 2.14 (b, 1H, OH), 1.89-0.95 (m, 84H, -CH₂-), 0.70 (t, 9H, -CH₃). Elemental analysis: calcd (%) for C₉₂H₁₄₆N₈O₈: C 74.05; H 9.86; N 7.51. Found: C 74.00; H 9.83; N 7.46. UV Vis (CH₂Cl₂), λ_{max} nm (logε): 703 (4.94), 669 (4.91), 640 (4.66), 612 (4.53), 389 (4.66), 345 (4.92).

A₃B type unsymmetrical nickel phthalocyanine (**A**₃**B**-**Ni**): Yield: 12% (0.033 g), FTIR (ATR), v/cm⁻¹: 3100-3600 (-OH), 3074 (Ar. C-H), 2918, 2850 (Al. C-H), 1610, 1531, 1485, 1466, (C=C, C=N), 1241, 1121, 1093, 1066 (C-O-C), 821, 750, 720. ¹H NMR (400 MHz, CDCl₃) (δ: ppm): 7.84-7.06 (m, 12H, Ar-H), 4.21- 4.04 (m, 22H, O-CH₂-CH₂-O, O-CH₂-CH₂), 2.05 (b, 1H, OH), 1.68-1.03 (m, 84H, -CH₂-), 0.86 (t, 9H, CH₃). Elemental analysis: calcd (%) for C₉₂H₁₄₄N₈O₈Ni: C 71.34; H 9.37; N 7.23. Found: C 71.30; H 9.36; N 7.20. UV Vis (CH₂Cl₂), λ_{max} nm (logɛ): 674 (4.64), 616 (4.29), 383 (4.15), 336 (4.54).

A₃B type unsymmetrical zinc phthalocyanine (A₃B-Zn): Yield: 10% (0.027 g), FTIR (ATR), v/cm⁻¹: 3100-3500 (-OH), 3071 (Ar. C-H), 2919, 2851 (Al. C-H), 1600, 1489, 1466 (C=C, C=N), 1291, 1231, 1081 (C-O-C). 749,719. ¹H NMR (400 MHz, CDCl₃) (δ: ppm): 7.78-7.16 (m, 12H, Ar-H), 4.27-3.56 (m, 22H O-CH₂-CH₂-O, O-CH₂-CH₂), 2.05 (b, 1H, OH), 1.87-1.02 (m, 84H, -CH₂-), 0.87 (t, 9H, -CH₃). Elemental analysis: calcd (%) for C₉₂H₁₄₄N₈O₈Zn: C 71.03; H 9.33; N 7.20. Found: C 70.98; H 9.30; N 7.16. UV Vis (CH₂Cl₂), λ_{max} nm (logε): 681 (5.19), 618 (4.47), 349 (4.88).

3. Results and discussion

3.1. Synthesis and characterization

In this study, five phthalocyanine compounds were synthesized. Two different phthalonitrile precursor molecules (**A** and **B**, in Scheme 1) were used for the synthesis. One of the precursors (**A**) has hydrophobic characteristic, while the other molecule has hydrophilic characteristic (**B**). And so, the formed phthalocyanines show amphiphilic characteristic. The synthesis of the similar phthalocyanines has been reported in the given references [38, 39]. The reason for using such compounds which have the opposite character is to facilitate the separation of the compounds during column chromatography experiments. Phthalocyanines

that were synthesized from the derivative of two different phthalonitriles to give six possible phthalocyanine products are A_4 , A_3B , AABB, ABAB, ABAB, AB₃, B_4 [40]. Statistical condensation method which is includes one different and three identical precursor compounds (in 3:1 molar ratios) was used for the higher yield gain of the A_3B type phthalocyanines in this study.

During the purification studies, the polarity of the solvent mixtures was increased as the purification process is ongoing so that more polar compounds were separated in different fractions. The first fraction gave only A₄ product, the second fraction gave A₃B product, and the other fractions gave the others (AABB, ABAB, AB₃, and B₄ which weren't the aim in this study).

A₃B type phthalocyanines were analyzed with different techniques and the results were found compatible with the targeted molecules (Scheme 1). UV Vis absorption spectroscopy is an effective technique for characterization of the phthalocyanines. Phthalocyanines are known for their two characteristic absorption bands in UV Vis spectrum: the Q band $(n \rightarrow \pi^*)$ in the visible region and Soret band (B bond, $\pi \rightarrow \pi^*$) in the near UV [41]. The Q band appears at approximately 600-750 nm and the B band appears at approximately 300-400 nm [42]. In the case of metal-free phthalocyanines, the Q band is divided into two [43]. In this context, all phthalocyanines which were synthesized in this study are consistent with provided information above. UV Vis spectra of all phthalocyanines (A₃B-Co, A₃B-Cu, A₃B-H, A₃B-Ni, and A₃B-Zn) were given in supplementary information (Fig. S. 9, Fig. S 10, Fig. S 11, Fig. S 12, and Fig. S 13, respectively). The table 1 summarizes the UV Vis information of synthesized phthalocyanines.



Scheme 1. Synthesis routes for the phthalonitriles (A and B) and phthalocyanines (A_3B -Co, A_3B -Cu, A_3B -H, A_3B -Ni, A_3B -Zn), (i) K₂CO₃, DMF, N₂, 15 h, 105 °C, (ii) K₂CO₃, DMF, N₂, 48 h, 45 °C, (iii) n-pentanol, DBU, N₂, 48 h, and reflux (common step for all Pcs), CoCl₂ (for A_3B -Co), CuCl₂ (for A_3B -Cu), NiCl₂ (for A_3B -H), Zn(OAc)₂ (for A_3B -Zn).

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$\textbf{Compound} \rightarrow$	A ₃ B-Co	A ₃ B-Cu	A ₃ B-H	A ₃ B-Ni	A ₃ B-Zn				
Q Bands	675 (5.24)	678 (4.97)	703 (4.94)	674 (4.64),	681 (5.19)				
nm (log ε)	615 (4.83)	623 (4.63)	669 (4.91)	616 (4.29),	618 (4.47)				
			640 (4.66)						
			612 (4.53)						
B Bands	357 (5.00)	387 (4.41)	389 (4.66)	383 (4.15)	349 (4.88)				
nm(log ε)		335 (4.77)	345 (4.92)	336 (4.54)					

Table 1. Absorption data for synthesized unsymmetrical phthalocyanines in CH₂Cl₂

The FTIR spectra of the compounds were given in Fig. S 1, Fig. S 2, Fig. S 3, Fig. S 4, and Fig. S 5 for A₃B-Co, A₃B-Cu, A₃B-H, A₃B-Ni, and A₃B-Zn, respectively. It was seen that the CN bands both at 2229 cm⁻¹ for A and 2225 cm⁻¹ for B were disappeared in all spectra after the phthalocyanine formation. It is a justification of the formation of the phthalocyanines in addition to the UV Vis spectra. In general, stretching vibration of the OH bond at between 3100 and 3600 cm⁻¹, aromatic protons at between 3068 and 3074 cm⁻¹, aliphatic protons at between 2917 and 2852 cm⁻¹, C=C and C=N double bonds at between 1610 and 1450 cm⁻¹, and different C-O bonds at between 1291 and 1052 cm⁻¹ appeared in all Pc compounds.

From the ¹H NMR spectra of the phthalocyanines, it is expected that the presence of aromatic protons in Pc ring, aliphatic protons in tetraethylene glycol and hexadecyl moieties, methyl protons of the end group in hexadecyl and methylene protons that adjacent to oxygen atoms, and hydroxyl proton. All of these were seen in the related spectra (Fig. S 6, Fig. S 7, and Fig. S 8) for **A₃B-H**, **A₃B-Ni**, **A₃B-Zn**, respectively. Signals of the aromatic protons appeared at approximately between 8.36 and 6.97 ppm as a multiplet, the signals of methylene protons which adjacent to the oxygen atoms are observed at between 4.48 and 4.03 ppm as a multiplet, hydroxyl proton's signal is seen at roughly 2.00 ppm as a broad peak, the signals of free methylene protons are observed at between 1.89 and 0.95 and lastly, end group CH₃'s signal is split into a triplet and is observed at approximately 0.70 ppm.

3.2. Aggregation studies

Aggregation which is also known as self-assembly is defined as the association of the phthalocyanines at changing ranges from dimers to oligomers [44]. The aggregation is classified in different types (D, H and J type aggregation) [45] depending on the size of the aggregation. It is an important and interesting property in many fields such as chemical and biochemical systems. The aggregation is one of the most important characteristics of phthalocyanines [46]. Phthalocyanines' aggregation limits their some properties such as photochemical activity [47, 48], nonlinear optical property [44], solubility, purification and characterization, the effectiveness in the PDT [49]. Aggregation depends on the nature of solvents and substituents, the metal ion in the phthahocyanine center, temperature, the concentration of the solution and it can be measured using various methods including electronic spectroscopy, fluorescence spectroscopy, nuclear magnetic resonance spectroscopy, vapor pressure osmometry, calorimetry, and the others [45]. Using the UV Vis spectroscopy is one of the most common methods in the determination of the aggregation as it can be seen in some studies [50-54].

The monomeric states of the metalled and metal-free phthalocyanines are representable with narrow and sharp bands in Q band region [55, 56]. When the phthalocyanines were aggregated, the Q band absorption broadens and decreases [57-59]. The D type aggregation is referred to dimeric species in the molecule and can be determined with decreased monomeric band intensity and a new band appearance on the short wavelength side of the visible spectrum; it looks like the equal two bands. H type aggregation (comes from hypsochromic shift) expresses the larger aggregation, and J type aggregation (comes from Jelley who discovered it) expresses the polymeric aggregation [45]. The former aggregation type (H) is recognizable with the shift toward to blue from the region of monomeric absorption bands, and the latter aggregation type (J) is known with the red-shift of the bands which belongs to monomeric species [60].

In this study, the aggregation behaviors depending on the solvents of the synthesized five phthalocyanines were examined via UV Vis spectroscopy. All phthalocyanines are soluble in tetrahydrofuran, cyclohexane, hexane, diethyl ether, chloroform, dichloromethane and pyridine and insoluble in common polar solvents such as water, methanol, ethanol, acetonitrile, acetone, ethyl acetate. For this reason, in the aggregation studies of the phthalocyanines were used in the former solvent groups. The solubility changed considerably

from polar solvents to apolar solvents when the phthalocyanine side chains transformed to three alkyl chains and one polyethylene glycol chain according to our previous study in which peg-substituted phthalocyanines were synthesized symmetrically [61].

In the context of explanations above and UV Vis spectra in different solvents of the phtalocyanines, the aggregation investigation results were given for each phthalocyanine below, A₃B-Co, A₃B-Cu, A₃B-H, A₃B-Ni, and A₃B-Zn, respectively.

A₃B-Co (Fig. 1): The phthalocyanine was found in the monomeric state in four solvent: diethyl ether, hexane, chloroform and pyridine, on the other hand we cannot say the same situation for tetrahydrofuran and cyclohexane solutions because of the deviation from specific spectrum which belongs to monomeric state. The phthalocyanine shows dimeric aggregation in tetrahydrofuran solution. Surprisingly, in the cyclohexane solution, we observed a red shifted band together with blue shifted bands. This unusual formation may occur in different solvents [62]. **A₃B-Cu** (Fig. 2): The phthalocyanine was found in non-aggregated form in pyridine, chloroform and tetrahydrofuran; whereas it was found in dimeric aggregation state in cyclohexane and diethyl ether. **A₃B-H** (Fig. 3): Unsymmetrical metal-free phthalocyanine protects its monomeric form in pyridine, chloroform, tetrahydrofuran and diethyl ether; on the other hand it forms dimeric aggregation in hexane and cyclohexane. **A₃B-Ni** (Fig. 4): Unsymmetrical nickel phthalocyanine complex shows aggregation formation in all solvents with the extended version of aggregation stats. **A₃B-Zn** (Fig. 5): The best result on behalf of the non-aggregation belongs to the zinc phthalocyanine because there was no aggregation formation in any solvents. It is the best candidate for further analyses.



Fig. 1. Aggregation behavior of A_3B -Co in different solvents at 5×10^{-5} M.



Fig. 2. Aggregation behavior of A_3B -Cu in different solvents at 5×10^{-5} M.



Fig. 3. Aggregation behavior of A_3B-H in different solvents at 5×10^{-5} M.



Fig. 4. Aggregation behavior of A_3B -Ni in different solvents at 5×10^{-5} M.



Fig. 5. Aggregation behavior of A_3B -Zn in different solvents at 5×10^5 M.

In this study, we also investigated the dependence on the concentration of aggregation behaviors of copper phthalocyanine and nickel phthalocyanine in five solvents, including chloroform, pyridine, tetrahydrofuran, diethyl ether, and cyclohexane. It was used eight different concentrations (in Fig. 6 and Fig. 7 for chloroform; in Fig.S 14-21 for the other solvents) for the investigations. Both phthalocyanines obeyed the Lambert-Beer Law in the mentioned concentrations ranges in chloroform, pyridine and tetrahydrofuran solutions. On the other hand, the deviations from the Lambert-Beer Law were observed both diethyl ether and cyclohexane due to aggregation formation similar to previous studies in all concentrations. Fig. 6 shows the absorption spectra of A_3B -Cu at different concentration values, respectively. Fig 7 shows the absorption spectra of A_3B -Ni at different concentrations and in chloroform. There, C1 and C8 indicate 2.03 x 10⁻⁵ and 4.5 x 10⁻⁶ concentration values, respectively.



Fig. 6. Absorption spectra of A_3B -Cu from C1 (4.06 x 10^{-5} M) to C8 (9.03 x 10^{-6} M) at eight different concentrations in chloroform.



Fig. 7. Absorption spectra of A_3B -Ni from C1 (2.03 x 10⁻⁵) to C8 (4.50 x 10⁻⁶) at eight different concentrations in chloroform.

3.3. Thermal analysis

Thermal analysis experiments were carried out in dry air atmosphere at 50 mL/min the purge gas flow rate and 20 °C/min heating rate, by using (DTG-60/60H)/TG/DTA simultaneous measuring instrument. Phthalocyanines were dried at 160 °C before analysis. Thermal analysis curves of the synthesized phthalocyanines were given in supplementary information from Fig. S 22 to Fig. S 26 for synthesized five compounds. According to the given curves, decomposition temperatures of the phthalocyanines were found higher than 250 °C. The minimum onset of decomposition temperature is 260 °C and maximum offset is 680 °C. All phthalocyanines were decomposed in two steps. First decomposition step belongs to the degradation of ligands (tetraethylene glycol and cetyl alcohol in the peripheral position of the phthalocyanines) and second decomposition step belongs to the degradation of Pc macrocyclics in all curves. Also, Thermogravimetric Analysis (TGA) curves are useful in the determination of the Pc/ligand ratios in the phthalocyanines. Table 2 gives comprehensive information about both theoretical and experimental results of % weight loss and the decomposition temperature ranges for both ligands and phthalocyanines.

	for ligands			for Pc ring				
	decomposition	% weight	% weight	decomposition	% weight	% weight		
	temperature	loss	loss	temperature	loss	loss		
	ranges (°C)	(found)	(calculated)	ranges (°C)	(found)	(calculated)		
A ₃ B-Co	329-531	58.45	59.05	531-650	36.37	36.89		
A ₃ B-Cu	336-534	59.53	59.00	534-650	37.12	37.00		
A ₃ B-H	260-489	61.60	61.49	489-590	37.70	38.51		
A ₃ B-Ni	320-510	58.86	59.23	510-678	36.73	36.87		
A ₃ B-Zn	320-505	58.15	58.98	505-680	37.18	37.15		

Table 2. Thermal analysis results for the synthesized five unsymmetric phthalocyanines.

Conclusions

In this study, five unsymmetrical A_3B type phthalocyanines (A_3B -Co, A_3B -Cu, A_3B -H, A_3B -Ni, and A3B-Zn) were synthesized from two different phthalonitrile derivatives (A and B). Substituents which have different characteristic (hydrophilic and hydrophobic) were preferred to do easier the purification and separation and so, to increase the yields of the products. Compounds were obtained relatively with good yields according to the unsymmetrical synthesis: 17%, 13%, 8%, 12%, and 10% in return for the given order above.

All compounds were analyzed via suitable analysis techniques including UV Vis, FTIR, ¹H NMR, ¹³C NMR, elemental analysis and thermal analysis. The solubility of the phthalocyanines was determined in common organic solvents. Aggregation behaviors of the phthalocyanines were examined in six solvents including chloroform, cyclohexane, diethyl ether, hexane, pyridine, tetrahydrofuran. **A₃B-Zn** was found that in the monomeric state in all solvents. The others protected their monomeric statuses in chloroform and pyridine solutions as a general result. Aggregation types of the compounds changed from dimeric to higher order complexes (except for **A₃B-Zn**) the most effective candidate was found **A₃B-Zn** about aggregation matter because there was no aggregation in any solvents. Thermal stabilities of the phthalocyanines were also examined. As anticipated, metal-free phthalocyanine was found more unstable than metalled phthalocyanines. Decomposition started at 260 °C for metal-free Pc and at 320 °C for metalled Pcs as a minimum onset temperature value.

Declaration of interest

Both authors affirm no conflict of interest.

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Highlights

- Preparation of the phthalonitrile derivatives and A₃B-type five phthalocyanines.
- Determination of the structures by spectroscopic and non-spectroscopic methods.
- Investigation of the aggregation statuses in different solvents.
- Determination of the thermal stabilities of all phthalocyanines.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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