

Synthesis of metal-free and metallophthalocyanines containing 18- and 21-membered macrocycles with mixed donor atoms and their metal-ion binding properties

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Abstract: This paper describes the synthesis of a series of metal-free phthalocyanines and metallophthalocyanines peripherally substituted by macrocycles of different ring sizes with the same donor atom sets. The effects of varying ring size of the macrocycle on the spectroscopic and metal ion binding properties of phthalocyanines were examined. For these purposes, electronic absorption properties for metal-free phthalocyanines and metallophthalocyanines were studied in dimethylformamide and tetrahydrofuran. The liquid–liquid extraction of metal picrates such as Ag(I), Hg(II), Cd(II), Zn(II), Cu(II), Ni(II), Pb(II), and Co(II) from the aqueous phase to the organic phase was carried out using metallophthalocyanines. All new compounds were characterized using several spectroscopic techniques.

Key words: Mixed-donor macrocycle, metal-free phthalocyanine, metallophthalocyanine, solvent extraction

1. Introduction

Phthalocyanines and their metal complexes are one of the most attractive functional molecular materials in the literature. They have been studied in detail for many years and are still receiving much attention because of their extraordinary properties. These compounds have found application as dyes and pigments^{1,2} and have potential as catalysts in Li-air batteries,³ in oxidation of aromatic compounds,⁴ as gas sensors,⁵ as Langmuir–Blodgett films,⁶ and as photosensitizers in photodynamic cancer therapy⁷ due to their unique properties such as high molar absorption coefficients, electron transfer abilities, and thermal and chemical stability.⁸ Factors such as the central metal and the nature and position of the substituents have an influence on their spectroscopic properties.^{9–12} Metallophthalocyanines containing diamagnetic metals such as zinc and silicon as central metal are well known in photodynamic therapy due to their high triplet state quantum yields.¹¹ Metallophthalocyanines with a redox active metal center such as cobalt, manganese, and titanium are used for the design of electrochemical sensors due to their electrocatalytic properties toward many analytes.^{11,13}

The usage of the phthalocyanine in applications is closely related to its molecular composition, stability, and solubility. The limited solubility of the phthalocyanine in common organic solvents is the major problem concerning its application capabilities. It is known that unsubstituted phthalocyanines are less soluble in common organic solvents than substituted phthalocyanines are.¹⁴ In order to improve the solubility of phthalocyanine in various solvents, many modifications to the peripheral or nonperipheral position of the phthalocyanines have been reported.^{15–20}

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One of these modifications is preparing phthalocyanines starting from a phthalonitrile precursor containing a macrocyclic unit. Incorporation of a macrocycle into the phthalocyanine ring affects the optical and electrochemical properties of phthalocyanines.^{21,22} A significant advantage of the attachment of a macrocycle with mixed donor atoms to the phthalocyanine ring, according to the HSAB concept, is that selectivity increases towards soft transition metal cations.²³ A series of closely related macrocyclic and macrobicyclic systems and their extractant properties were reported by Ocaik and co-workers. They demonstrated that the presence of soft donor atoms in the macrocyclic system enhanced the selective extraction for soft metal ions such as silver(I) and mercury(II).^{24–26} Several papers related to the synthesis of phthalocyanines containing macrocycles with different types of donor atoms were reported by Kantekin et al.^{27–30} One of those studies reported new soluble phthalocyanines containing a macrocyclic unit and investigation of their extraction properties towards metal ions.²⁷ They obtained the highest extraction values for silver(I), mercury(II), and cadmium (II) in the extraction experiments. They concluded that this was because sulfur containing ligands are especially appropriate for complexation with heavy metal cations such as silver(I), mercury(II), and cadmium (II) due to the softness of sulfur, which is in agreement with the HSAB concept. The synthesis of macrocycles of different ring sizes with different types of donor atoms and their extractant properties have been well studied.^{24–26,31–33} In contrast, mixed donor macrocycles substituted phthalocyanines and their metal-ion binding properties have been studied less.

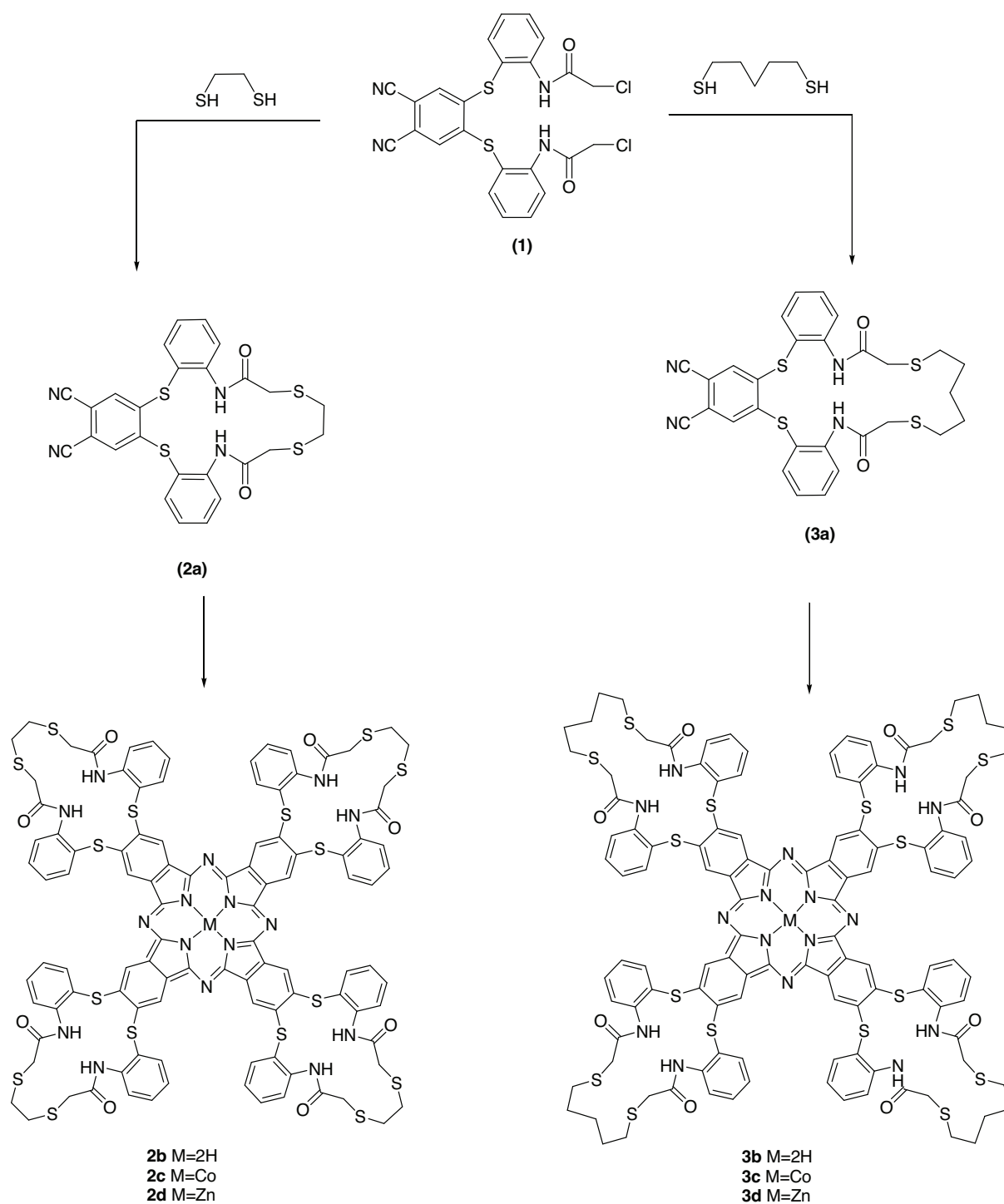
Our studies focused on selective and effective extraction of heavy metals and precious metals from solution and determining the extraction behavior of macrocycles in liquid–liquid medium. For these purposes, we have previously reported a series of synthesis of macrocycles and their metal ion binding properties in solvent extraction.^{31,34} The present study, as our ongoing research in this area, describes the synthesis and characterization of a series of metal-free phthalocyanines and metallophthalocyanines containing 18- and 21-membered macrocycles with mixed donor atoms. The effects of varying ring sizes of the macrocycle on the spectroscopic properties of phthalocyanines were examined. Cation extraction studies with synthesized phthalocyanines were performed using solvent extraction to evaluate the metal ion binding properties of phthalocyanines.

2. Results and discussion

2.1. Synthesis and characterization

Metal-free phthalocyanines **2b**–**3b** and metallophthalocyanines **2c**–**3c** and **2d**–**3d** were prepared by the route shown in Scheme 1. The structures of the novel compounds were characterized by a combination of elemental analysis and ¹H NMR, IR, UV-Vis, and MS spectral data. N,N'-(2,2'-(4,5-dicyano-1,2-phenylene)bis(sulfanediyl)bis(2,1-phenylene))bis(2-chloroacet-amide) **1** was employed as the starting material for the synthesis of phthalonitriles **2a** and **3a**.

The synthesis of metal-free phthalocyanines **2b** and **3b** from corresponding phthalonitriles **2a** and **3a** was accomplished in dry *n*-pentanol at reflux temperature for 24 h under argon in a Schlenk tube to afford **2b** and **3b** as dark green amorphous solids after purification by silica gel chromatography. The metal-free phthalocyanines were soluble in DMF and DMSO. The synthesis of metallophthalocyanines **2c**–**3c** and **2d**–**3d** with four macrocycles was achieved by treating the corresponding phthalonitrile precursors **2a** and **3a** with anhydrous Co(CH₃CO₂)₂ in quinoline for cobalt phthalocyanine complexes **2c**–**3c** and anhydrous Zn(CH₃CO₂)₂ in the same solvent for zinc phthalocyanine complexes **2d**–**3d**. All synthesized phthalocyanine derivatives were first treated with ethanol for 4 h under reflux temperature in a Soxhlet extractor, and then purified by silica gel chromatography using CH₂Cl₂:CH₃OH (95:5). The complexes were soluble in solvents such as DCM, DMF, and DMSO.



Scheme 1. The synthetic route of metal-free phthalocyanines **2b–3b** and metallophthalocyanines **2c–3c** and **2d–3d**.

Comparison of the ^1H NMR, IR, UV-Vis, and MS spectral data at each step gave some evidence of the formation of the target products. The IR spectra of the synthesized phthalocyanines are very similar. After conversion of the dinitrile precursors **2a** and **3a** to the phthalocyanines, the sharp $\text{C}\equiv\text{N}$ vibration around 2230 cm^{-1} in the IR spectra of phthalonitriles **2a** and **3a** disappeared in the IR spectra of the phthalocyanine

derivatives. IR spectra of all phthalocyanines are very similar and indicated the aromatic groups at around 3050 cm^{-1} , the aliphatic groups at around 2900 cm^{-1} , the C=O group at around 1680 cm^{-1} , and the NH groups in the macrocyclic rings at around 3280 cm^{-1} by intense bands. The only difference in the IR spectra of the metal-free phthalocyanines and metallophthalocyanines is a NH stretching band peak at around 3300 cm^{-1} due to the inner core of all metal-free phthalocyanines. The inner core -NH protons of the metal-free phthalocyanines are expected to be observed upfield around $\delta -3.00$ to -6.00 ppm in the ^1H NMR spectra.³⁵ The -NH protons of the metal-free phthalocyanines **2b** and **3b** were observed at around $\delta = -3.00$ ppm in their ^1H NMR spectra.

The ^1H NMR spectra of **2b–3b** and **2d–3d** exhibited aromatic protons at 9.14 (m, 8H, ArH), 7.50–6.85 (m, 32H, ArH) for **2b**, 9.01 (m, 8H, ArH), 7.63–6.86 (m, 32H, ArH) for **3b**, 8.70 (m, 8H, ArH), 8.04–6.93 (m, 32H, ArH) for **2d** and 8.58 (m, 8H, ArH), 7.55 (m, 32H, ArH) for **3d**. The resonance of the NH protons of the amide group in **2b–3b** and **2d–3d** appeared at around $\delta = 10.00$ ppm as a singlet in their ^1H NMR spectra. The ^1H NMR spectra of phthalocyanine derivatives **2b–3b** and **2d–3d** displayed broad peaks. It has been shown before that the extensive overlapping of the numerous protons in large phthalocyanine causes the broad peaks.³⁶ The ^1H NMR spectra of symmetric metal-free phthalocyanines **2b–3b** and metallophthalocyanines **2d–3d** in DMSO- d_6 exhibit the characteristic resonances of the macrocyclic and phthalocyanine moieties. All signals in the ^1H NMR spectra of metal-free phthalocyanines **2b–3b** and metallophthalocyanines **2d–3d** are identical to those of the corresponding phthalonitriles **2a** and **3a**.

The results of elemental analysis were in good agreement with the proposed structures of metallophthalocyanine derivatives **2c–3c** and **2d–3d**, but some of the metal-free phthalocyanines failed to afford satisfactory elemental analysis. On the other hand, elemental analyses of large Pc molecules sometimes give unsatisfactory results.^{36–38} Acquired MALDI-TOF spectra of the phthalocyanine derivatives allowed us to record molecular ion peaks at 2252.70 $[\text{M} + \text{H}]^+$ (**2c**), 2257.70 $[\text{M} + \text{H}]^+$ (**2d**), 2420.53 $[\text{M} + \text{H}]^+$ (**3c**), and 2425.09 $[\text{M} + \text{H}]^+$ (**3d**), confirming the proposed structures (Figure 1). All attempts to obtain molecular ion peaks for the metal-free phthalocyanines **2b** and **3b** using different matrixes (2,5-dihydroxybenzoic acid (DHB) or dithranol) in MALDI-TOF and different technique such as LC-MS failed. However, the UV-Vis, IR, and ^1H NMR spectroscopies for these two metal-free phthalocyanines **2b** and **3b** gave reasonable results confirming the identities of the structures.

2.2. Absorption properties

The UV-Vis absorption spectra of metal-free phthalocyanines **2b–3b** in DMF and THF are shown in Figures 2a and 2b. The Q band of the metal-free phthalocyanines splits into two bands in the visible region as a result of D_{2h} symmetry.^{39,40} The resolution of the split of the Q band decreases with increasing wavelength and the presence of aggregated phthalocyanine species in solution.^{41–44} In the case of the UV-Vis spectrum of metal-free phthalocyanines **2b–3b** recorded in DMF, the Q band was observed without splitting at 740 and 744 nm, respectively. The large red shift or presence of aggregated species must have resulted in an unsplit Q band.^{41,45,46} In the case of the UV-Vis spectra of metal-free phthalocyanines **2b–3b** recorded in THF, the UV-Vis spectra of metal-free phthalocyanines **2b–3b** gave unclear split Q bands in the visible region at around 719–741 nm as expected. Attempts to record UV-Vis spectra with clear split Q bands for the metal-free phthalocyanines **2b–3b** failed due to the insolubility of metal-free phthalocyanines **2b–3b** in other common organic solvents.

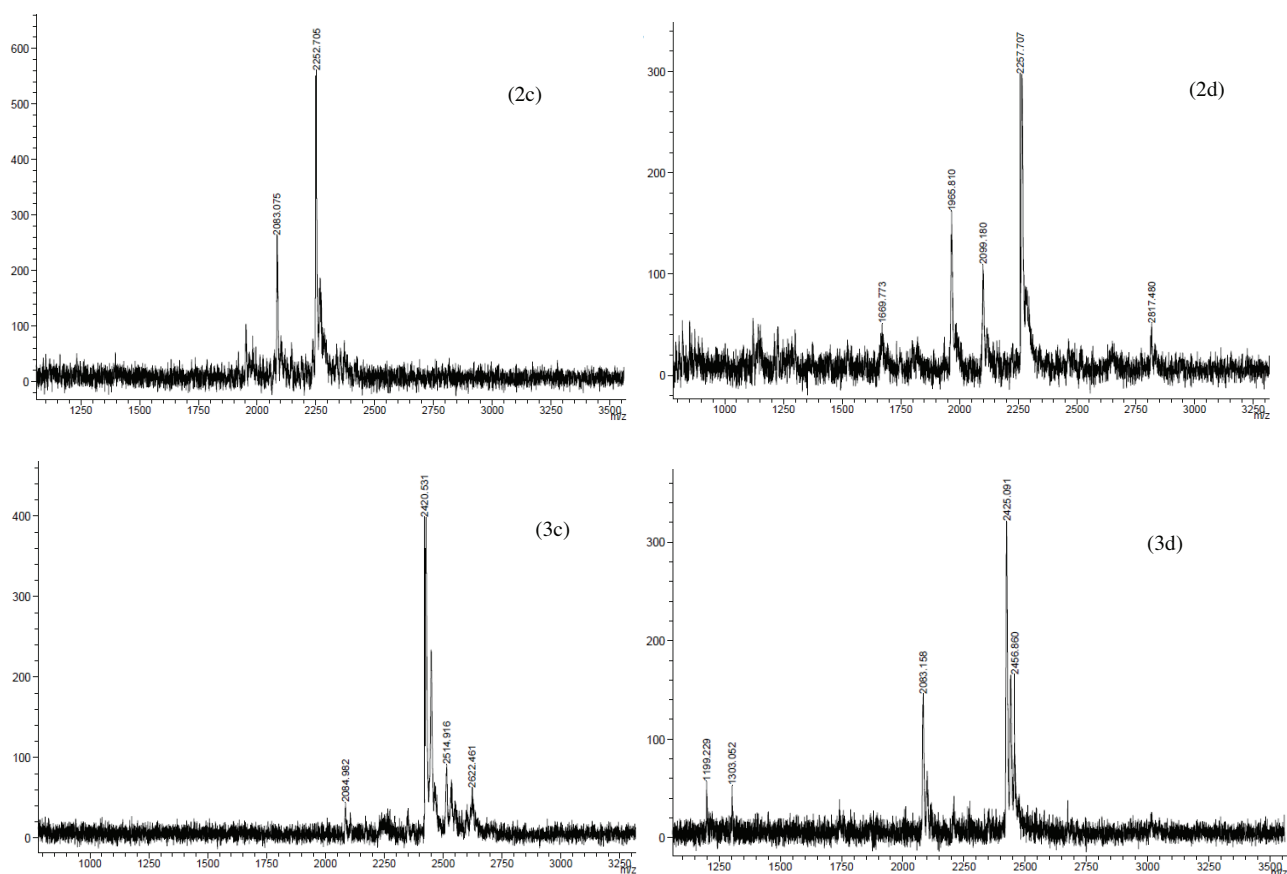


Figure 1. The MALDI-TOF spectra of metallophthalocyanines.

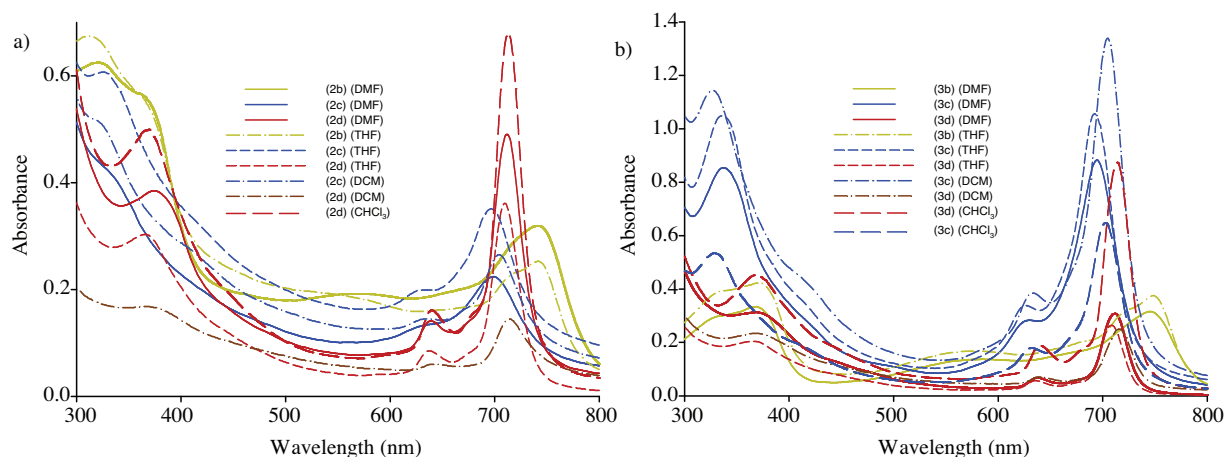


Figure 2. Absorption spectra of phthalocyanines **2b–2d** (a) and **3b–3d** (b) in different solvents.

Figures 2a and 2b also show the electronic spectra of metallophthalocyanines **2c–3c** and **2d–3d** in DMF, CH_2Cl_2 , and THF. Deprotonation of metal-free phthalocyanines and binding metal ion to inner core forms metallophthalocyanines with D_{4h} symmetry. Metal complexes of substituted and unsubstituted phthalocyanines with D_{4h} symmetry show an intense single Q band in the visible region.^{36,47} In the electronic spectra of cobalt(II) phthalocyanines **2c–3c** in DMF and THF, intense Q band absorptions were observed at around 692

nm with a weaker absorption at around 627 nm. The electronic spectra of zinc(II) phthalocyanines **2d–3d** display intense Q bands in the visible region at around 710 nm in DMF and THF with a weaker absorptions at around 640 nm. B band absorptions were observed at around 335 nm for cobalt(II) phthalocyanines **2c–3c** and 370 nm for zinc phthalocyanines **2d–3d** in DMF and THF. The values of Q and B band absorptions with molar absorption coefficients for all phthalocyanines are given in Table 1.

Table 1. Location of the Q bands and B bands (in nm) of metal-free phthalocyanines **2b–6b** and metallophthalocyanines **2c–6c** and **2d–6d** in DMF and THF.

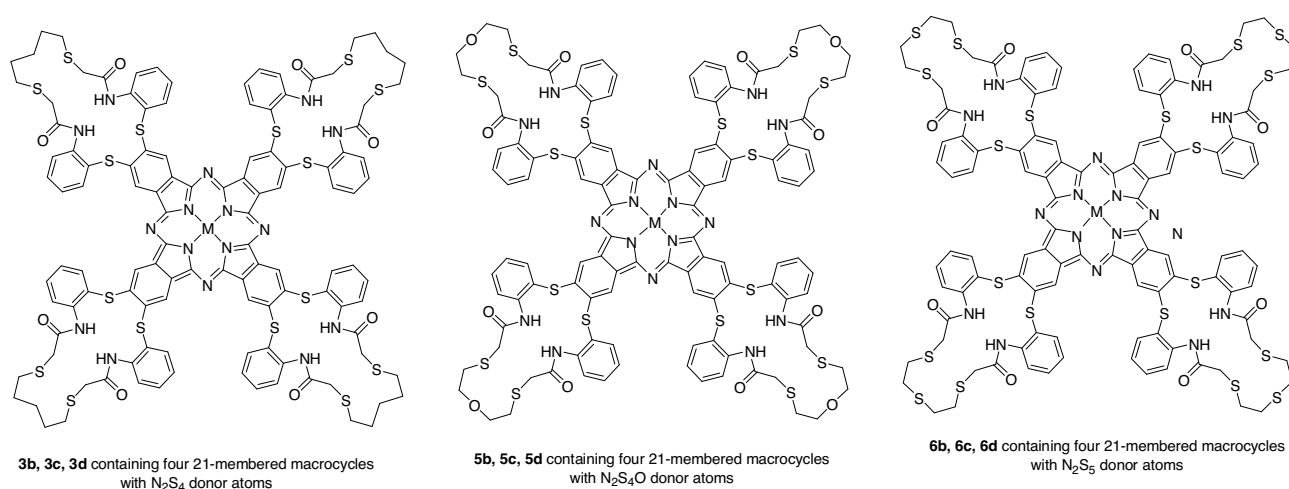
Pcs	Q band, λ_{\max} , (nm) (DMF)	Log ϵ	B band, λ_{\max} , (nm) (DMF)	Log ϵ	Q band, λ_{\max} , (nm) (THF)	Log ϵ	B band, λ_{\max} , (nm) (THF)	Log ϵ
2b	740	4.87	365, 319	5.13, 5.18	741, 718	4.62, 4.58	312, 360	5.05, 4.95
3b	744	5.15	366, 329	5.24, 5.21	741, 718	4.96, 4.90	332, 364	5.07, 5.01
4b ⁵⁵	743	5.10	366, 330	5.20, 5.18	741, 720	4.88, 4.82	332, 364	5.22, 5.22
5b ⁵³	743	5.06	364, 324	5.21, 5.23	741, 718	5.02, 4.96	320, 362	5.23, 5.19
6b ⁵⁴	745	4.71	367, 327	4.98, 5.02	741, 719	4.59, 4.57	328, 360	4.82, 4.81
2c	697, 629	4.75, 4.27	317	5.07	696, 631	4.64, 4.40	325	4.88
3c	691, 626	5.16, 4.67	340	5.15	692, 627	4.96, 4.46	336	4.95
4c ⁵⁵	692, 625	5.19, 4.74	336	5.19	692, 627	4.91, 4.44	333	4.94
5c ⁵³	694, 629	5.17, 4.70	338	5.17	692, 627	4.99, 4.50	335	5.00
6c ⁵⁴	695, 634	4.98, 4.58	335	5.05	692, 628	4.86, 4.38	335	4.88
2d	712, 640	5.35, 4.76	368	5.24	710, 638	4.67, 4.06	366	4.61
3d	711, 637	5.01, 4.29	368	4.72	709, 636	4.53, 3.85	366	4.42
4d ⁵⁵	711, 637	5.24, 4.54	369	4.95	708, 636	4.65, 3.96	365	4.51
5d ⁵³	711, 637	5.44, 4.80	372	5.15	709, 636	4.92, 4.22	369	4.65
6d ⁵⁴	713, 639	4.94, 4.33	376	4.82	709, 637	4.85, 4.20	368	4.72

The UV-Vis spectra of metallophthalocyanines **2c–3c** and **2d–3d** displayed a similar-shaped Q band, but with a small shift in the wavelength (Figure 2). This can be attributed to the molecular structure of metallophthalocyanines, which share a macrocycle peripherally substituted on the phthalocyanine ring but have different central metal ions such as zinc and cobalt for **2c–3c** and **2d–3d**, respectively. This structural similarity leads to the similar shapes of their Q-bands.⁴⁸

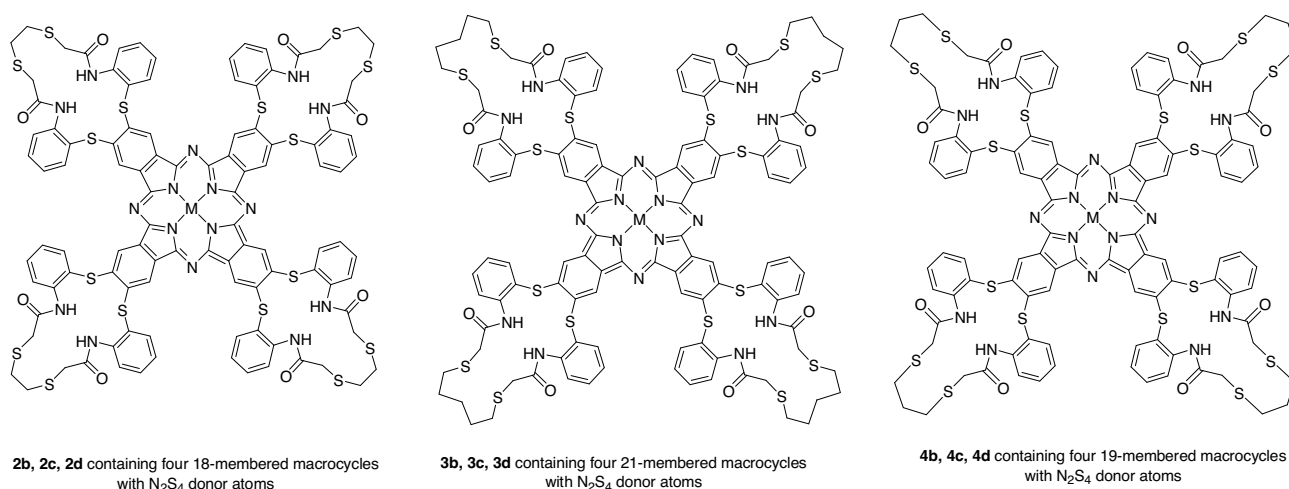
The Q band wavelength of the metallophthalocyanines **2c–3c** and **2d–3d** varies as the solvent is changed. The effects of solvents on the state of aggregation of soluble phthalocyanines have been studied by several groups and reported in numerous papers.^{49–52} The position of the Q band is affected by the polar solvents clearly shown by the shift of the Q band to shorter wavelengths and by a decrease in their molar absorptivity.^{49,50} Small shifts to shorter wavelength in the position of Q bands in the UV-Vis spectra of metallophthalocyanines were observed with increasing solvent polarity (Figure 2).

The effects of varying ring sizes of the macrocycle on the spectroscopic properties of phthalocyanines peripherally substituted by macrocycles were investigated. In the case of phthalocyanine derivatives **2b–2d** and **3b–3d**, which are substituted by four 18- and 21-membered macrocycles with N₂S₄ donor atoms, respectively (Scheme 1), it was observed that the Q band position for the metal-free phthalocyanines **2b–3b** and metallophthalocyanines **2c–3c** and **2d–3d** was constant at around 740, 690, and 710 nm, respectively. A series of structurally similar phthalocyanines **5b–5d** and **6b–6d** bearing 21-membered macrocycles peripherally with different types of donor atoms reported before by our group showed similar results for the Q band

positions (Scheme 2).^{53,54} When comparing the phthalocyanines **5b–5d** and **6b–6d** with the phthalocyanines **3b–3d**, phthalocyanine derivatives **5b–5d** and **6b–6d** contain one more oxygen and sulfur donor atoms, respectively, instead of one carbon atom in the phthalocyanines **3b–3d**. In the case of phthalocyanine derivatives **2b–2d**, **3b–3d**, and **4b–4d**, which are substituted by four 18-, 19-, and 21-membered macrocycles with N_2S_4 donor atoms, respectively (Scheme 3), they all have the same phthalocyanine skeleton substituted different ring-sized macrocycles at peripheral positions.⁵⁵ The Q band position for these structurally related phthalocyanine derivatives was observed at around 740 nm for metal-free phthalocyanines, 690 nm for cobalt(II) phthalocyanines, and 710 nm for zinc(II) phthalocyanines (Table 1). These results imply that changing one atom in the same macrocycle or varying ring sizes of the macrocycle containing the same number and type of donor atoms do not significantly affect the Q band position in these phthalocyanine derivatives.



Scheme 2. Phthalocyanine derivatives **3b–3d**, **5b–5d**, and **6b–6d** containing four 21-membered macrocycles.



Scheme 3. Phthalocyanine derivatives containing four macrocycles of different ring sizes: **2b–2d** with 18-membered macrocycle, **3b–3d** with 21-membered macrocycle, and **4b–4d** with 19-membered macrocycle.

2.3. Extraction of metal picrates

The metal ion binding properties of *N,N'*-(2,2'-(4,5-dicyano-1,2-phenylene)bis(sulfanediyl)bis(2,1-phenylene))bis(2-chloroacet-amide) **1**, cobalt(II) phthalocyanines **2c–3c**, and zinc(II) phthalocyanines **2d–3d** were determined by using solvent extraction experiments in order to estimate the extractability of metal ions such as Ag^+ , Hg^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , and Co^{2+} from the aqueous phase to the organic phase. The metal ion-binding properties of phthalonitriles **2a** and **3a** were reported before.³¹ Chloroform was tested as the organic solvent to reveal extraction efficiency. The results related to the extractability of the above metal picrates from aqueous phase to organic phase are given in Table 2 and illustrated in Figure 3.

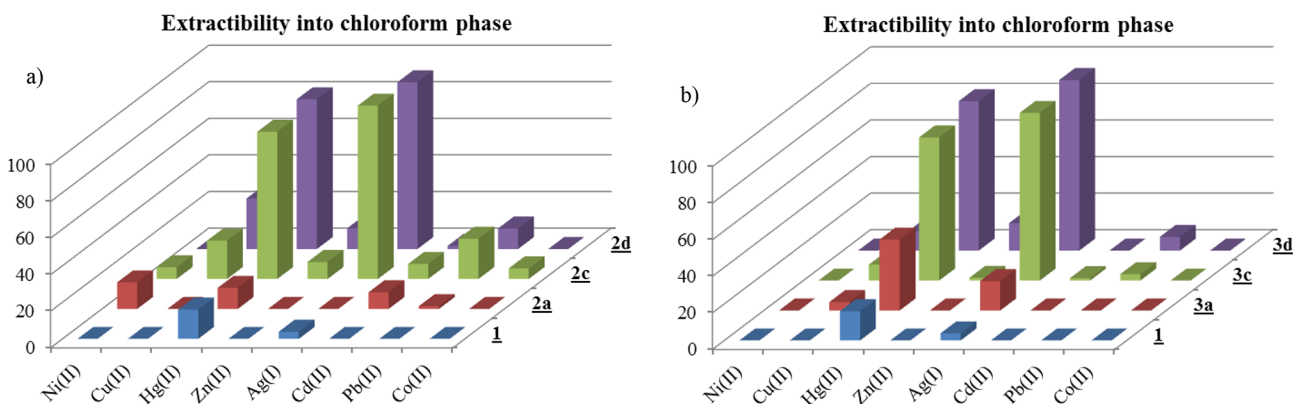


Figure 3. The extractability of aqueous metal picrates for **1**, **2a**, **2c**, **2d** (a) and **1**, **3a**, **3c**, **3d** (b) into the chloroform phase.

Table 2. The extractability of aqueous metal picrates for all compounds into the chloroform phase.

Metal ion	Extractability ^a (%)						
	(1)	(2a)	(3a)	(2c)	(2d)	(3c)	(3d)
Ni^{2+}	< 1	14.5 ± 0.2	< 1	6.4 ± 0.4	< 1	< 1	< 1
Cu^{2+}	< 1	0	4.6 ± 0.6	20.9 ± 1.3	27.6 ± 0.9	8.7 ± 0.7	10.7 ± 1.0
Hg^{2+}	16.0 ± 2.2	11.5 ± 0.3	38.8 ± 1.7	80.5 ± 1.5	81.9 ± 2.9	78.3 ± 1.7	81.7 ± 0.3
Zn^{2+}	0	0	0	9.3 ± 1.4	11.3 ± 1.9	1.5 ± 0.5	15.0 ± 1.8
Ag^+	3.9 ± 0.5	9.1 ± 0.6	16.1 ± 0.9	94.8 ± 1.5	91.2 ± 1.6	91.7 ± 0.3	93.3 ± 0.7
Cd^{2+}	< 1	< 1	< 1	8.2 ± 1.6	1.7 ± 0.1	1.3 ± 0.3	< 1
Pb^{2+}	< 1	1.5 ± 0.3	0	22.0 ± 0.3	11.2 ± 0.3	3.5 ± 0.3	7.5 ± 0.3
Co^{2+}	< 1	0	< 1	5.8 ± 1.4	< 1	< 1	< 1

^a Temperature: 20.0 ± 0.1 °C; aqueous phase (10 mL); $[\text{Pic}^-] = 1.25 \times 10^{-5}$ M, organic phase (10 mL); $[\text{L}] = 1.25 \times 10^{-4}$ M; the values calculated from three independent extraction experiments.

As seen from Table 2, precursor acetamide compound **1** with an open ring exhibited the lowest extraction efficiency for all the metal ions in chloroform. The best extractability belongs to the Hg^{2+} ion in chloroform by 16.0%. The reaction of precursor acetamide compound **1** with appropriate dithiol afforded phthalonitriles **2a** and **3a**, which are 18- and 21-membered macrocycles with N_2S_4 donor atoms, respectively. Both of the macrocycles possess the same number and type of donor atoms in the macrocyclic ring but have different cavity size. The 18-membered macrocycle with nitrogen sulfur donor atoms **2a** extracted Ag^+ and Hg^{2+} ions to the organic phase with 9.1% and 11.5%, respectively. The extraction values obtained in the presence of phthalonitrile

3a for Ag^+ and Hg^{2+} in chloroform were relatively high when compared to those of compounds **1** and **2a**. It extracted Ag^+ and Hg^{2+} ions to the chloroform phase with 16.1% and 38.8%, respectively. Cation binding properties depend upon different factors such as macrocyclic effect, cavity size, and the type and number of donor atoms.^{56,57} The high extraction efficiency in the presence of macrocycles compared to the results in the case of precursor acetamide **1** with an open ring can be interpreted as the result of the macrocyclic effect and the increment in the size of the macrocycles.

As seen from Scheme 1, all phthalocyanine derivatives contain either four 18-membered macrocycles (**2b**, **2c**, **2d**) or four 21-membered macrocycles (**3b**, **3c**, **3d**). The E% values obtained for metal cation extraction with all phthalocyanines were higher than those of phthalonitriles **2a** and **3a** in organic solvent. The highest extractability belongs to Hg^{2+} and Ag^+ cations with all phthalocyanines (**2c**, **2d**, **3c**, **3d**) in organic solvent. The values of extractability belonging to Hg^{2+} and Ag^+ are in the range of 91.2%–94.8% and 78%–81%, respectively. This showed that the extraction capabilities of the phthalocyanine containing macrocycles increase compared to those of corresponding macrocycles.

The systematic changes in macrocyclic ligands' structures such as variation in donor atom sets and the macrocyclic cavity size have certain effects on macrocycle selectivity towards metal ions.⁵⁸ Table 3 contains a comparison of the results of the current study with those of previous studies for cation-macrocycle interaction for Ag(I) and Hg(II) metal ions with a series of closely structures containing macrocycles.^{27,59,60} The extraction values given in Table 3 referred to the conditions when the macrocycles were attached to either a phthalocyanine or porphyrazine skeleton. As seen clearly from Table 3, the extraction results for Ag(I) and Hg(II) metal ions obtained from different studies with a series of closely structures showed similar behavior. It can be concluded that the increasing extraction capability is due to the planarity of phthalocyanines and porphyrazines skeleton and increasing number of the macrocyclic unit in phthalocyanines and porphyrazines.

Table 3. The extractability values of Ag^+ and Hg^{2+} ions with a series of closely related ligands.

Ring size	Donor atom sets	% Extractability		Reference
		Ag(I)	Hg(II)	
19-membered	N_2S_4	91%	81%	This study
21-membered	N_2S_4	92%	80%	This study
16-membered	NS_5	93%	65%	[27]
14-membered	S_2O_2	95%	89%	[59]
14-membered	S_4	94%	86%	[59]
18-membered	S_2O_4	94%	81%	[60]

Consequently, new metal-free phthalocyanines and metallophthalocyanines containing macrocycles in different ring sizes were synthesized and characterized. Comparison of the λ_{max} of the phthalocyanine derivatives **2b**–**3b**, **2c**–**3c**, and **2d**–**3d** in different solvents such as DMF and THF illustrated no sensitivity of the Q band to varying ring size of macrocycle substituted phthalocyanines. From the experimental results of the solvent extraction, all phthalocyanines showed high extraction efficiency towards Hg^{2+} and Ag^+ cations. They are all excellent extractors for those cations and have the potential to be used in the efficient extraction of Ag^+ and Hg^{2+} ions from aqueous solutions.

3. Experimental

3.1. Materials

N,N'-(2,2'-(4,5-dicyano-1,2-phenylene)bis(sulfanediyl)bis(2,1-phenylene))bis(2-chloroacetamide) **1** and phthalonitriles **2a** and **3a** were prepared according to the literature.^{31,53} All reagents and solvents were reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego.⁶¹

Chloroform, dichloromethane, picric acid, $\text{Pb}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, AgNO_3 , and $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ were reagent grade quality and were purchased from Merck. Demineralized water was used in the extraction experiments. The solvents were saturated with each other before use in order to prevent volume changes of the phases during extraction.

3.2. Equipment

FTIR spectra were measured on a PerkinElmer Spectrum 65 spectrometer in KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer in CDCl_3 and DMSO-d_6 (99.9%). Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS and a Bruker Daltonics MALDI-TOF spectrometer. Optical spectra were recorded in the UV-Vis region with a PG T80+ spectrophotometer in 1 cm path length cuvettes at room temperature. The elemental analyses were conducted with a LECO Elemental Analyzer (CHNS 0932) spectrophotometer. The melting points were determined with an electrothermal apparatus and are reported without correction. In the solvent extraction experiment, a Selecta type shaker with a thermostat was used.

3.3. Synthesis

3.3.1. General procedure for the syntheses of metal-free phthalocyanines (**2b**, **3b**)

A mixture of an appropriate phthalonitrile [**2a** (0.250 g, 0.455 mmol) and **3a** (0.3 g, 0.505 mmol)] and a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry *n*-pentanol (1.5 mL) was placed under a nitrogen atmosphere in a standard Schlenk tube. The reaction mixture was heated and was stirred under nitrogen at 145 °C for 24 h. After cooling to room temperature, the mixture was diluted with ethanol (10 mL) until the product precipitated. The precipitated crude product was filtered and then treated with ethanol for 4 h in a Soxhlet extractor. It was then filtered and washed with ethanol, diethyl ether, and CH_2Cl_2 and was dried under a vacuum. Finally, pure metal-free phthalocyanines were obtained by silica gel chromatography using $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ (95:5).

3.3.2. Metal-free phthalocyanine (**2b**)

The yield was 32% (0.082 g). mp > 300 °C. Anal. calcd. for $\text{C}_{104}\text{H}_{82}\text{N}_{16}\text{O}_8\text{S}_{16}$: C, 56.86; H, 3.76; N, 10.20%. Found: C, 55.59; H, 3.84; N, 10.13. IR (KBr disc) $\nu_{\text{max}}/\text{cm}^{-1}$: 3381 (NH), 3284 (NH), 3051 (CH_{Ar}), 2924 (CH), 1642 (C=O), 1575, 1510, 1467, 1338, 1302, 1259, 1106, 1021, 871, 742, 678. ^1H NMR (DMSO-d_6) δ : 10.11 (br, s, 8H, NH), 9.14 (m, 8H, ArH), 7.50–6.85 (m, 32H, ArH), 3.53 (br, s, 16H, O=C– CH_2), 2.63 (br, s, 16H, SCH_2), –2.97 (br, s, 2H, NH). UV-Vis (DMF): λ_{max} , nm (log ϵ): 740 (4.87), 589 (4.81), 365 (5.13), 319 (5.18).

3.3.3. Metal-free phthalocyanine (3b)

The yield was 22% (0.066 g). mp > 300 °C. Anal. calcd. for C₁₁₆H₁₀₆N₁₆O₈S₁₆: C, 58.91; H, 4.52; N, 9.48%. Found: C, 54.36; H, 3.68; N, 10.51. IR (KBr disc) $\nu_{\max}/\text{cm}^{-1}$: 3385 (NH), 3285 (NH), 3047 (CH_{Ar}), 2907 (CH), 1671 (C=O), 1606, 1575, 1508, 1477, 1437, 1378, 1302, 1259, 1106, 1019, 871, 737, 677. ¹H NMR (DMSO-d₆) δ : 10.01 (br, s, 8H, NH), 9.01 (m, 8H, ArH), 7.63–6.86 (m, 32H, ArH), 3.58 (br, s, 16H, O=C–CH₂), 2.74 (m, 16H, SCH₂), 1.75–1.60 (m, 24H, SCH₂), –3.55 (br, s, 2H, NH). UV-Vis (DMF): λ_{\max} , nm (log ϵ): 744 (5.15), 589 (4.86), 366 (5.24), 329 (5.21).

3.3.4. General procedure for the syntheses of metallophthalocyanines (2c–3c, 2d–3d)

Phthalonitrile [**2a** (0.3 g, 0.546 mmol) and **3a** (0.3 g, 0.505 mmol)] was reacted with anhydrous Co(CH₃CO₂)₂ and Zn(CH₃CO₂)₂ in quinoline (2 mL) at 190 °C for 7 h in a Schlenk tube under nitrogen in order to obtain cobalt(II) phthalocyanines **2c–3c** and zinc(II) phthalocyanines **2d–3d**, respectively. At the end of this period, the reaction mixture was cooled to room temperature. The product was precipitated by the addition of ethanol (10 mL) and the product was filtered. The crude product was treated with ethanol for 4 h in a Soxhlet extractor. The green product was then filtered and washed with ethyl acetate, acetone, and diethyl ether. Finally, pure phthalocyanines were obtained by silica gel column chromatography using CH₂Cl₂:CH₃OH (95:5).

3.3.5. Cobalt(II) phthalocyanine (2c)

The yield was 40% (0.133 g). mp > 300 °C. Anal. calcd. for C₁₀₄H₈₀N₁₆O₈S₁₆Co: C, 55.42; H, 3.58; N, 9.94%. Found: C, 54.68; H, 3.85; N, 9.63. IR (KBr disc) $\nu_{\max}/\text{cm}^{-1}$: 3290 (NH), 3051 (CH_{Ar}), 2914 (CH₃), 1681 (C=O), 1578, 1515, 1435, 1409, 1380, 1297, 1122, 1064, 958, 755. ¹H UV-Vis (DMF): λ_{\max} , nm (log ϵ): 697 (4.75), 629 (4.27), 317 (5.07). MS (MALDI-TOF) m/z: 2252.70 [M + H]⁺.

3.3.6. Cobalt(II) phthalocyanine (3c)

The yield was 63% (0.190 g). mp > 300 °C. Anal. calcd. for C₁₁₆H₁₀₄N₁₆O₈S₁₆Co: C, 57.27; H, 4.33; N, 9.25%. Found: C, 57.65; H, 4.78; N, 8.84. IR (KBr disc) $\nu_{\max}/\text{cm}^{-1}$: 3279 (NH), 3058 (CH_{Ar}), 2924 (CH₃), 2861, 1683 (C=O), 1578, 1514, 1435, 1408, 1379, 1298, 1118, 1070, 959, 755. UV-Vis (DMF): λ_{\max} , nm (log ϵ): 691 (5.16), 626 (4.67), 340 (5.15). MS (MALDI-TOF) m/z: 2420.53 [M + H]⁺, 2514.91 [M + 4Na]⁺.

3.3.7. Zinc(II) phthalocyanine (2d)

The yield was 20% (0.060 g). mp > 300 °C. Anal. calcd. for C₁₀₄H₈₀N₁₆O₈S₁₆Zn: C, 55.26; H, 3.57; N, 9.91%. Found: C, 54.58; H, 3.70; N, 9.54. IR (KBr disc) $\nu_{\max}/\text{cm}^{-1}$: 3270 (NH), 3055 (CH_{Ar}), 2918 (CH₃), 1665 (C=O), 1577, 1512, 1434, 1370, 1296, 1111, 1062, 938, 756. ¹H NMR (DMSO-d₆): δ 10.17 (br, s, 8H, NH), 8.70 (m, 8H, ArH), 8.04–6.93 (m, 32H, ArH), 3.51 (br, s, 16H, O=C–CH₂), 3.11 (br, s, 16H, SCH₂). UV-Vis (DMF): λ_{\max} , nm (log ϵ): 712 (5.35), 640 (4.76), 368 (5.24). MS (MALDI-TOF) m/z: 2257.70 [M + H]⁺.

3.3.8. Zinc(II) phthalocyanine (3d)

The yield was 16% (0.048 g). mp > 300 °C. Anal. calcd. for C₁₁₆H₁₀₄N₁₆O₈S₁₆Zn: C, 57.37; H, 4.32; N, 9.23%. Found: C, 53.44, H, 4.70; N, 8.45. IR (KBr disc) $\nu_{\max}/\text{cm}^{-1}$: 3278 (NH), 3058 (CH_{Ar}), 2924 (CH₃), 2852, 1660 (C=O), 1578, 1512, 1434, 1372, 1298, 1110, 1062, 939, 756. ¹H NMR (DMSO-d₆): δ 10.06 (br, s, 8H, NH), 8.58 (m, 8H, ArH), 7.55 (m, 32H, ArH), 3.33 (br, s, O=CH₂Cl), 2.66 (m, 16H, SCH₂), 1.65 (m, 24H, SCH₂). UV-Vis (DMF): λ_{\max} , nm (log ϵ): 711 (5.01), 637 (4.29), 368 (4.72). MS (MALDI-TOF) m/z: 2425.09 [M + H]⁺.

3.4. Extraction method

The metal ion binding properties of N,N'-(2,2'-(4,5-dicyano-1,2-phenylene)bis(sulfanediyl)bis(2,1-phenylene))bis(2-chloroacet-amide) **1**, cobalt(II) phthalocyanines **2c–3c**, and zinc(II) phthalocyanines **2d–3d** were investigated by liquid–liquid solvent extraction. Picrate extraction experiments were performed following published procedures.^{31–34,62} Solvent extraction experiments were carried out using aqueous metal picrate solutions, which were prepared from a mixture of the metal nitrates (Pb(NO₃)₂, Co(NO₃)₂.6H₂O, Cu(NO₃)₂.3H₂O, Zn(NO₃)₂.6H₂O, Ni(NO₃)₂.6H₂O, Cd(NO₃)₂.4H₂O, AgNO₃, Hg(NO₃)₂.H₂O) and picric acid in deionized water. Chloroform was tested as organic solvent in extraction experiments. An organic solution (10 mL) of ligand (1.25 × 10⁻⁴ M) and an aqueous solution (10 mL) containing 1.25 × 10⁻⁵ M picric acid and 1 × 10⁻² M metal nitrate were placed in stoppered flask and shaken for 2 h at 20 ± 0.1 °C. Then the resulting mixtures were allowed to stand for least 2 h at that temperature in order to complete the phase separation. The concentration of the picrate ion remaining in the aqueous phase was then determined by UV-Vis spectrophotometer at 355 nm. A blank experiment was performed in the absence of host and showed that no picrate extraction occurred.

The extractability (E %) was determined as the absorbance of picrate in aqueous solutions. The extractability was calculated from the following equation:

$$E(\%) = \frac{[A_0 - A]}{A_0} \times 100, \quad (1)$$

where A_0 is the absorbance in the absence of ligand and A the absorbance in the aqueous phase after extraction.

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