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# Synthesis and characterization of metal-free phthalocyanine containing 16-membered $N_2S_2$-donor macrocycles linked to a 2-pyridinyl methyl moiety

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ABSTRACT

A metal-free phthalocyanine (**$H_2$Pc**) containing four diazadithiamacrocycles a with 2-pyridinyl methyl groups attached was synthesized via cyclotetramerization of 4,5-*bis*{2-[13(2-pyridinylmethyl)-1, 9-dithia-5,13-diazacyclohexadecanyl-5]ethyl} thiophthalonitrile in the presence of DBU as a strong organic base. New compounds were characterized by a combination of elemental analysis, $^1$H NMR, $^{13}$C NMR, IR, UV/vis, and MS spectral data.



Phthalocyanines and related compounds have diverse optical, electronic, and co-ordination properties and have attracted considerable attention.[1] Phthalocyanine chemistry has undergone a renaissance as these compounds and their derivatives exhibit singular and unconventional properties. Their interesting applications include: Langmuir–Blodgett films, electrochromic display devices, gas sensors, liquid crystals, nonlinear optics, and photodynamic therapy (PDT).[2] Unsubstituted phthalocyanines are colored materials, but they are not generally soluble in common organic solvents. However, substitution of the peripheral positions of the phthalocyanines with appropriate functional groups improves their solubility and increases their effectiveness in many applications.[3] When functional groups such as sulfonates, carboxylates, and quaternized amino or pyridine groups are attached to the peripheral position of the phthalocyanine structure, the solubility of such compounds can be improved significantly in protic solvents.[4]

The synthesis of relatively small sized macrocycles such as $N_4$ and $S_4$ donor sets has been well examined.[5] In contrast, sulfur and nitrogen mixed donor macrocycles have been less studied.[6] A significant advantage of these types of macrocycles is their ability to behave as selective metal extraction agents for soft metal cations such as cadmium, mercury, and silver, and as models for the active sites of some enzymes.[7] *N*-Functionalization of these macrocycles may enhance their metal-ion selectivity and the stability of metal complexes depending on the coordination properties of the pendant arms. Additionally, macrocyclic complexes with pendant arms have shown interesting properties as probes and model molecules in biochemical processes. Metal complexes with pendant-armed mixed-donor macrocyclic ligands have been designed as models of electron transport and activation in biological systems, and as chemical models of hydrolytic metalloenzymes. Such compounds may have various photochemical applications, for example, the photocatalyzed reduction of $CO_2$ and/or the removal of industrial pollutants like sulfides. Moreover, *N*-pyridyl derivatives of macrocyclic compounds and their complexes are soluble in organic media, and they mediate effective membrane transport of alkaline-earth and some transition metal cations.[8]

In our laboratory, we have focused on the synthesis of mixed-donor macrocycles connected to a tetrapyrrolic skeleton. Considering that introduction of a pyridine moiety to the macrocyclic backbone is expected to increase the stereochemical rigidity of the resulting complexes, to provide functionalization toward specific targets, we decided to study a metal-free phthalocyanine in which are attached 16-membered mixed-donor macrocycles with pendant pyridine moieties. The combination of the two different groups is expected to result in co-ordination of transition metal ions (Scheme 1).

Reaction of 2 equiv of 3-chloro-1-propanol (**1**) and $Na_2CO_3$ with 2-(aminomethyl)pyridine (**2**) in dry acetonitrile at reflux temperature under a argon atmosphere for five days afforded

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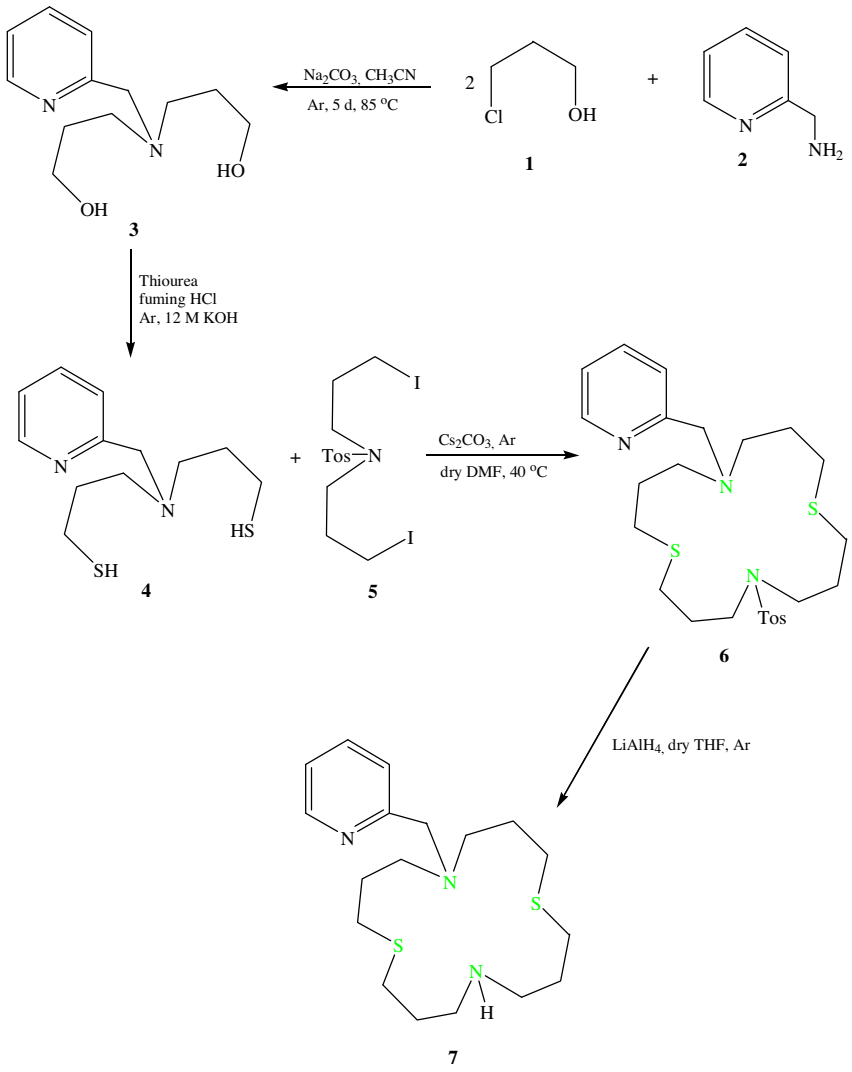
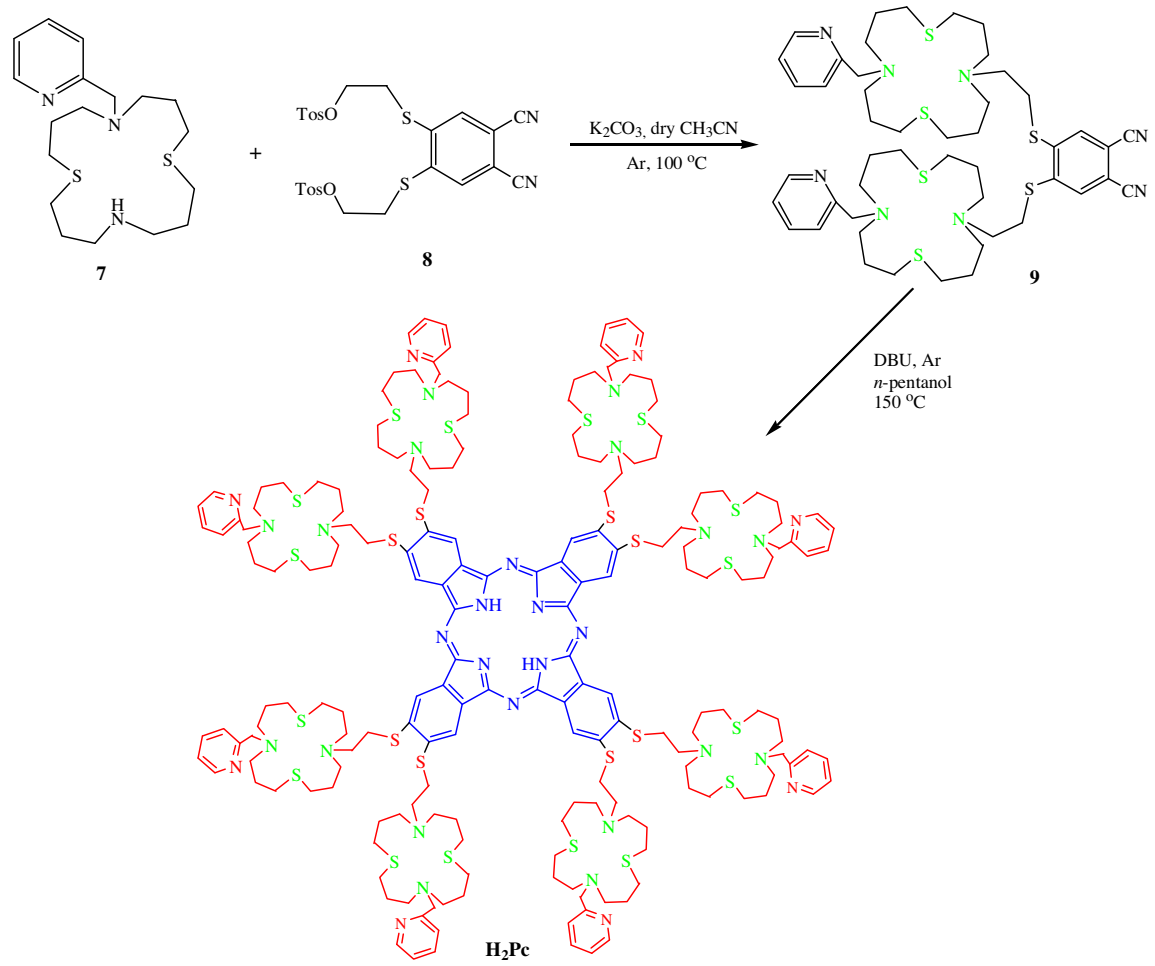



**Scheme 1.** The synthesis of pendant-armed 16-membered mixed donor ($N_2S_2$) macrocycle **7**.

3,3′-(pyridin-2-ylazanediyl)bis(propan-1-ol) (**3**)[9] in ca. 82% yield. The EI mass spectrum of **3** exhibited a molecular ion peak at *m*/*z* = 225 $[M+1]^+$, which supported the structure. The $^1H$ NMR spectrum of **3** showed signals due to aromatic, $OCH_2$, and OH protons at $\delta$ 8.41–7.08, $\delta$ 3.90–3.47, and $\delta$ 4.82, respectively. The $^{13}C$ NMR spectrum of the same compound clearly indicated the presence of pyridine, pyridine-connected $CH_2$, $NCH_2$, and $OCH_2$ resonances at $\delta$ 159.72–123.06, $\delta$ 52.87, $\delta$ 60.05, and $\delta$ 62.19, respectively. The absence of $NH_2$ and the presence of OH stretching vibrations in the IR spectrum also confirmed the formation of **3**. The conversion of **3** into the mercapto derivative **4**[10] was achieved in 26% yield by reaction with thiourea and fuming HCl at reflux temperature for 20 h, followed by cooling to room temperature, dropwise addition of 12 M KOH solution and then refluxing for 3 h. Product **4** displayed the expected molecular ion peak at *m*/*z* = 257 $[M+1]^+$. In the $^1H$ and $^{13}C$ NMR spectra of **4**, the characteristic resonances of the aromatic protons and carbons were very similar to those of **3**. The signal at $\delta$ 2.60 corresponding to the $H_2C$–SH protons was identified easily by deuterium exchange. The proton-decoupled $^{13}C$ NMR spectrum of this compound showed resonances due to the $H_2C$–SH groups at $\delta$ 30.98. The stretching vibrations at 2544 $cm^{-1}$ representing SH groups in the IR spectrum of this compound also confirmed the formation of **4**.

Treatment of **4** with diiodide **5**[11] in dry DMF in the presence of $Cs_2CO_3$ using a high dilution technique resulted in the formation of the desired diazadithiamacrocycle **6**[12] in 64% yield, the structure of which was confirmed by elemental analysis and from spectral data. This compound contained a tosyl moiety as was substantiated by the two characteristic doublets at $\delta$ 7.65 and $\delta$ 7.30 in the $^1H$ NMR spectrum. The resonances belonging to the SH protons in the precursor compound **4** were absent after the macrocyclization reaction, as expected. The molecular ion peak at *m*/*z* = 508 $[M]^+$ together with appropriate ion fragments were in good accord with the suggested structure. The detosylated macrocycle **7**[13] was prepared in 62% yield by reaction of **6** with excess $LiAlH_4$. After removal of the tosyl group from **6**, the NH group was observed in the $^1H$ NMR spectrum at $\delta$ 1.58.[6e] The proton-decoupled $^{13}C$ NMR spectrum of this compound displayed characteristic signals of the product. The disappearance of the stretching vibration of the tosyl group at 1596 $cm^{-1}$ and the presence of N–H absorptions at 3296 $cm^{-1}$ in the IR spectrum of **7** also confirmed that detosylation had occurred. A molecular ion peak was observed at *m*/*z* = 354.20 $[M+1]^+$ in the mass spectrum.

Macrocycle **7** was reacted with phthalonitrile **8**[14] in the presence of $K_2CO_3$ in refluxing dry acetonitrile to give the corresponding dicyano compound. Purification by column chromatography [silica gel (chloroform)] afforded **9**[15] in 68% yield, for which




**Scheme 2.** Synthesis of the metal-free phthalocyanine (**$H_2$Pc**).

elemental analysis and ESI mass spectral data were satisfactory: 951.41 $[M+1]^+$. In the IR spectrum of **9**, an intense stretching vibration at 2229 $cm^{-1}$ corresponded to the C≡N groups. A singlet at $\delta$ 7.53 and multiplet at $\delta$ 2.77 in the $^1H$ NMR spectrum corresponded to the tetrasubstituted aromatic group and the $SCH_2$ groups, respectively. The carbon resonances belonging to the phthalonitrile group at $\delta$ 136.36, $\delta$ 127.48, $\delta$ 115.41, and $\delta$ 112.64 were in agreement with the target compound (Scheme 2).

Condensation of four moles of phthalonitrile **9** to give the metal-free phthalocyanine **$H_2$Pc**[16] was carried out in dry pentanol in the presence of the nonnucleophilic base, DBU.[17] The metal-free phthalocyanine was obtained in 11% yield, as a dark green solid, after purification by column chromatography [silica gel (chloroform)]. In the IR spectrum of this compound, a diagnostic feature of the formation of **$H_2$Pc** from **9** was the disappearance of the sharp C≡N signals and the presence of C=N stretching vibrations at 1641 $cm^{-1}$. The $^1H$ NMR spectrum of the symmetric metal-free phthalocyanine exhibited characteristic chemical shifts for the pendant arms and the macrocyclic moieties. This spectrum closely resembled that of the precursor **9**, as expected. The deuterium exchangeable inner core protons could not be observed in the $^1H$ NMR spectrum of **$H_2$Pc** due to the high aggregation ability of this type of compounds.[18] In the $^{13}C$ NMR spectrum of **$H_2$Pc**, a resonance was observed at $\delta$ 155.27 corresponding to the C=N groups.

The UV/vis absorption spectra of a solution of **$H_2$Pc** in chloroform, DMF, and DMSO at room temperature are given in Figure 1. The split Q-band, which is characteristic of a metal-free phthalocyanine derivative was observed at $\lambda_{max}$ = 727 and 703 nm due to an electronic transition from the π-HOMO to the π*-LUMO energy level.[19] This intense Q-bands in compound **$H_2$Pc** indicated a monomeric species with $D_{2h}$ symmetry.[20] The **$H_2$Pc** absorption spectrum showed the expected splitting of the band at 727 and 703 nm, which can be attributed to the monomeric species of this compound.[21] The split Q-band absorptions in chloroform are due to the $\pi \rightarrow \pi^*$ transition of this fully conjugated 18π electron system.[22] The lower energy (red-shifted) band at 670 nm was due to the monomeric species. The metal-free phthalocyanine did not show significant aggregation behavior in $CHCl_3$, but it exhibited a small amount of aggregation in DMF and somewhat more in DMSO than DMF due to the coordination ability of these solvents,[23] as judged by the broadening and blue-shifting of the Q band. The presence of strong absorption bands in the UV region at $\lambda_{ma}$ = 347 nm was indicative of the Soret band due to electronic transitions from deeper $\pi \rightarrow \pi^*$ levels.

In conclusion, we have reported the synthesis of metal free phthalocyanines bearing eight 16-membered $N_2S_2$ each with an *N*-pyridin-2-ylmethyl substituent. This compound is promising as selective metal extractant. The synthesized molecule possesses a versatile funtionalization pattern for further coupling to a wide range of derivatives. Despite its strong hydrophobicity, it could be dissolved in water for biological investigations. Based on the results presented in this Letter, we are now designing metal extraction studies and related derivatives with improved hydrophilicity.

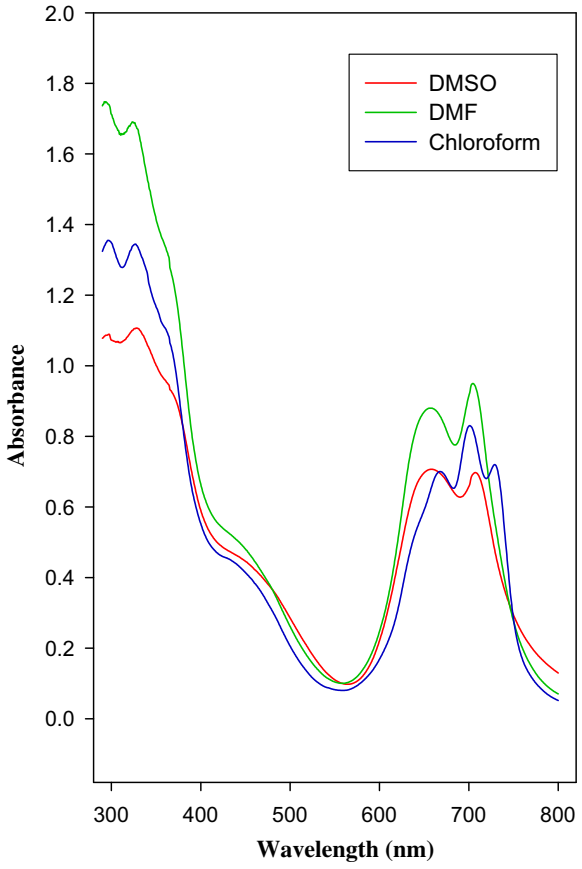



**Figure 1.** UV/vis spectra ($1 \times 10^{-5}$ M in $CHCl_3$, DMF, and DMSO) of **$H_2$Pc**.

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## References and notes


1. (a)*Phthalocyanines: Properties and Applications*; Lezznoff, C. C., Lever, A. B. P., Eds.; VCH: Weinheim, 1989, 1993, 1996; Vols. 1–4, (b) Moser, F. H.; Thomas, A. L. *The Phthalocyanines: Properties* In ; CRC Press: Boca Raton, Florida, 1983; Vol. 1,
2. (a) de la Torre, G.; Vazquez, P.; Agullo-Lopez, F.; Torres, T. *J. Mater. Chem.* **1998**, *8*, 1671–1683; (b) Cook, M. J.; Dunn, A. J.; Daniel, F. M.; Hart, R. C. O.; Richardson, R. M.; Roser, S. J. *Thin Solid Films* **1998**, *159*, 395–404; (c) Guillaud, G.; Simon, J.; Germain, J. P. *Coord. Chem. Rev.* **1998**, *180*, 1433–1484; (d) Durmuş, M.; Nyokong, T. *Photochem. Photobiol. Sci.* **2007**, *6*, 659–668; (e) Claessens, C. G.; Blau, W. J.; Cook, M. J.; Hanack, M.; Nolte, R. J. M.; Torres, T.; Wöhrle, D. *Monatsh. Chem.* **2001**, *132*, 3–11; (f) Ben-Hur, E.; Rosenthal, I. *Photochem. Photobiol.* **1985**, *42*, 129–133; (g) Martinez-Diaz, M. V.; de la Torre, G.; Torres, T. *Chem. Commun.* **2010**, 7090–7108; (h) Wang, A.; Long, L.; Zharg, C. *J. Inclusion Phenom. Macrocycl. Chem.* **2011**, *71*, 1–24; (i) Walter, M. G.; Rudine, A. B.; Wamser, C. C. *J. Porphyrins Phthalocyanines* **2010**, *14*, 759–792; (j) Ogura, S.-I.; Tabaka, K.; Fukushima, K.; Kamachi, T.; Okura, I. *J. Porphyrins Phthalocyanines* **2006**, *10*, 1116–1124.
3. (a) Ahsen, V.; Yılmazer, E.; Erbaş, M.; Bekaroğlu, Ö. *J. Chem. Soc., Dalton Trans.* **1988**, 401–406; (b) Eberhardt, W.; Hanack, M. *Synthesis* **1995**, 95–100; (c) Leznoff, C. C.; Marcuccio, S. M.; Greenberg, S.; Lever, A. B. P.; Tomer, K. B. *Can. J. Chem.* **1985**, *63*, 623–632; (d) Dumoulin, F.; Durmuş, M.; Ahsen, V.; Nyokong, T. *Coord. Chem. Rev.* **2010**, *254*, 2792–2847.
4. (a) Ogunsipe, A.; Nyokong, T. *J. Photochem. Photobiol., A* **2005**, *173*, 211–220; (b) Kahl, S. B.; Li, J. *Inorg. Chem.* **1996**, *35*, 3878–3880; (c) de Filippis, M. P.; Dei, D.; Fantetti, L.; Roncucci, G. *Tetrahedron Lett.* **2000**, *41*, 9143–9147.
5. (a) Melson, G. A. Coordination Chemistry of Macrocyclic Compounds In Melson, G., Ed.; Plenum Press: New York, 1979; (b) Bradshaw, J. S.; Krakowiak, K. E.; Izatt, R. M. *Aza-crown macrocycles*; John Wiley & Sons: New York, 1993; (c) Gerbeleu, N. V.; Arion, V. B.; Burgess, J. *Template Synthesis of Macrocyclic Compounds*; Wiley-VCH: Weinheim, 1999.
6. (a) Black, D. S. C.; McLean, L. A. *J. Chem. Soc., Chem. Commun.* **1968**, 1004–1005; (b) Westerby, B. C.; Juntunen, K. L.; Leggett, G. H.; Pett, V. B.; Koenigbauer, M. J.; Purgett, M. D.; Taschner, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1991**, *30*, 2109–2120; (c) Krylova, K.; Kulatilleke, C. P.; Heeg, M. J.; Salhi, C. A.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1999**, *38*, 4322–4328; (d) Siegfried, L.; Kaden, T. A. *Helv. Chim. Acta* **1984**, *67*, 29–38; (e) Groth, A. M.; Lindoy, L. F.; Meenhan, G. V. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1553–1558; (f) Chartres, J. D.; Lindoy, F. L.; Meenhan, G. V. *Tetrahedron* **2006**, *62*, 4173–4187; (g) Chak, B. C. M.; McAuley, A. *Can. J. Chem.* **2006**, *84*, 187–195; (h) Gök, Y.; Karaböcek, S. *Z. Anorg. Allg. Chem.* **1995**, *621*, 654–658; (i) Kabay, N.; Gök, Y. *Inorg. Chem. Commun.* **2011**, *14*, 1880–1883; (j) Glenny, M. W.; van de Water, L. G. A.; Vere, J. M.; Blake, A. J.; Wilson, C.; Driessen, W. L.; Reedijk, J.; Schröder, M. *Polyhedron* **2006**, *25*, 599–612.
7. (a) Ishikawa, J.; Sakamoto, H.; Nakamura, M.; Doi, K.; Wada, H. *J. Chem. Soc., Dalton Trans.* **1999**, 191–200; (b) Sakamoto, H.; Ishikawa, J.; Otomo, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2831–2836; (c) Glenny, M. W.; van de Water, L. G. A.; Driessen, W. L.; Reedijk, J.; Blake, A. J.; Wilson, C.; Schröder, M. *Dalton Trans.* **2004**, 1953–1959; (d) Krylova, K.; Kulatilleke, C. P.; Heeg, M. J.; Salhi, C. A.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1999**, *38*, 4322–4328.
8. (a) Chak, B.; McAuley, A.; Whitcombe, T. W. *Inorg. Chim. Acta* **1996**, *246*, 349–360; (b) Marques, F.; Guerra, K. P.; Gano, L.; Costa, J.; Campello, M. P.; Lima, L. M. P.; Delgado, R.; Drew, M. G. B.; Felix, V. *Dalton Trans.* **1999**, 4331–4339.
9. Compound **3**: brown oil. IR (NaCl disc, $cm^{-1}$): 3391, 3013, 2935–2856, 1654: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.41 (d, $J$ = 4.8, 1H, PyH), 7.58 (t, $J$ = 8.6, 1H, PyH), 7.21 (t, $J$ = 8.0, 1H, PyH), 7.08 (d, $J$ = 2.4, 1H, PyH), 4.82 (br, 2H, OH), 3.90–3.47 (m, 6H, $PyCH_2$, $OCH_2$), 2.50 (t, $J$ = 12.8, 4H, $NCH_2$), 1.60 (t, $J$ = 11.6, 4H, $CH_2$): $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 159.72, 149.89, 137.72, 124.00, 123.06, 62.19, 60.05, 52.87, 29.20: Anal. Calcd. for $C_{12}H_{20}N_2O_2$: C, 64.28; H, 8.93; N, 12.51. Found: C, 64.37; H, 9.26; N, 12.32. MS (EI) $m/z$: 225 $[M+1]^+$.
10. Compound **4**: pale yellow oil. IR (NaCl disc, $cm^{-1}$): 3059, 2930–2864, 2544, 1668: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.60 (d, $J$ = 3.6, 1H, PyH), 8.00 (s, 1H, PyH), 7.80 (d, $J$ = 1.2, 1H, PyH), 7.17 (t, $J$ = 7.8, 1H, PyH), 3.95 (s, 2H, $PyCH_2$), 3.25 (t, $J$ = 14.8, 2H, SH), 2.85 (m, 4H, $NCH_2$), 2.60 (m, 4H, $SCH_2$), 2.22 (m, 4H, $CH_2$): $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.16, 149.33, 137.30, 125.77, 124.02, 51.42, 36.82, 30.98, 21.38: Anal. Calcd. for $C_{12}H_{20}N_2S_2$: C, 56.25; H, 7.81; N, 10.93. Found: C, 55.96; H, 7.60; N, 11.23. MS (EI): $m/z$ 257 $[M+1]^+$.
11. Kabay, N.; Gök, Y. *Supramol. Chem.* **2011**, *23*, 641–644.
12. Compound **6**: pale orange oil. IR (NaCl disc, $cm^{-1}$): 3061, 3023, 2925–2868, 1596, 1338: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 8.50 (d, $J$ = 6.3, 1H, PyH), 8.01 (s, 1H, PyH), 7.65 (d, $J$ = 8.2, 2H, ArH), 7.42 (t, $J$ = 7.6, 1H, PyH), 7.30 (d, $J$ = 8.2, 2H, ArH), 7.10 (d, $J$ = 6.5, 1H, PyH), 4.18 (s, 2H, $PyCH_2$), 3.70 (m, 4H, $NCH_2$), 3.20 (m, 4H, $NCH_2$), 2.85 (m, 8H, $SCH_2$), 2.50 (s, 3H, $CH_3$), 2.10 (m, 8H, $CH_2$). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ 160.23, 150.36, 145.39, 137.03, 130.10, 128.08, 124.26, 122.45, 62.51, 53.36, 48.30, 42.21, 35.56, 22.16: Anal. Calcd. for $C_{25}H_{37}N_3S_3O_2$: C, 59.17; H, 7.29; N, 8.28. Found: C, 59.43; H, 7.01; N, 8.05. MS (EI) $m/z$: 508 $[M]^+$.
13. Compound **7**: yellow oil. IR (NaCl disc, $cm^{-1}$): 3296, 3061, 3013, 2925–2853, 1640: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 8.54 (s, 1H, PyH), 8.04 (d, $J$ = 8.2, 1H, PyH), 7.52 (d, $J$ = 7.9, 1H, PyH), 7.14 (m, 1H, PyH), 4.14 (s, 2H, $PyCH_2$), 3.71 (m, 4H, $NCH_2$), 3.58 (m, 4H, $NCH_2$), 2.75 (m, 8H, $SCH_2$), 2.10 (m, 8H, $CH_2$), 1.58 (s, 1H, NH). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$: 159.21, 148.74, 138.35, 127.48, 124.50, 59.25, 54.11, 43.52, 34.04, 30.91, 28.68. Anal. Calcd. for $C_{18}H_{31}N_3S_2$: C, 61.18; H, 8.78; N, 11.89. Found: C, 60.93; H, 8.63; N, 11.76. MS (EI) $m/z$ = 354 $[M+1]^+$.
14. Gürek, A.; Bekaroğlu, Ö. *J. Porphyrins Phthalocyanines* **1997**, *1*, 1077–1080.
15. Compound **9**: waxy solid. IR (NaCl disc, $cm^{-1}$): 3073, 3058, 2925–2854, 2229, 1659: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 8.51 (m, 2H, PyH), 8.01 (m, 2H, PyH), 7.53 (s, 2H, ArH), 7.48 (m, 2H, PyH), 7.21 (m, 2H, PyH), 4.19 (m, 4H, $PyCH_2$), 3.78 (m, 10H, $NCH_2$), 3.61 (m, 10H, $NCH_2$), 2.77 (m, 20H, $SCH_2$), 1.99 (m, 16H, $CH_2$). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ 161.17, 148.13, 136.36, 130.02, 128.23, 127.48, 124.50, 115.41, 112.64, 58.31, 53.29, 42.95, 34.04, 29.64, 28.41. Anal. Calcd. for $C_{48}H_{70}N_8S_6$: C, 60.63; H, 7.36; N, 11.78. Found: C, 60.91; H, 7.59, N, 11.53. MS (ESI) $m/z$ = 951.41 $[M+1]^+$.
16. Compound **$H_2$Pc**: solid, mp >300 °C. IR (KBr disc, $cm^{-1}$): 3290, 3084, 3051, 2924–2856, 1641. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 8.46 (m, 8H, PyH), 7.97 (m, 8H, PyH), 7.68 (s, 8H, ArH), 7.45 (m, 8H, PyH), 7.26 (m, 8H, PyH), 4.25 (m, 16H, $PyCH_2$), 3.75 (m, 40H, $NCH_2$), 3.58 (m, 40H, $NCH_2$), 2.65 (m, 80H, $SCH_2$), 2.01 (m, 64H, $CH_2$). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$: 160.76, 155.27, 147.91, 136.79, 129.63, 128.01, 127.12, 124.97, 116.85, 58.82, 53.78, 43.25, 34.41, 29.11, 28.93. Anal. Calcd. for $C_{192}H_{282}N_{32}S_{24}$: C, 60.59; H, 7.41; N, 11.78. Found: C, 60.35; H, 7.68; N, 11.51. UV/vis [$CHCl_3$, $\lambda_{max}$/nm ($\log\varepsilon$)]: 727 (4.14), 703 (4.23), 670 (4.00), 347 (5.23).
17. (a) Wöhrle, D.; Ekser, M.; Shigehara, K.; Yamada, A. *Synthesis* **1993**, 194–196; (b) Yıldız, S. Z.; Kantekin, H.; Gök, Y. *J. Porphyrins Phthalocyanines* **2001**, *5*, 367–375; (c) Kantekin, H.; Değirmencioğlu, I.; Gök, Y. *Acta Chem. Scand.* **1999**, *53*, 247–252.
18. (a) van Nostrum, C. F.; Picken, S. J.; Schouten, A. I.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1995**, *117*, 9957–9965; (b)*Phthalocyanines Properties and Applications*; Stillman, M. J., Nyokong, T., Eds.; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1989; Vol. 1, pp 133–289.
19. Bayrak, R.; Akçay, H. T.; Durmuş, M.; Değiermencioglu, I. *J. Organomet. Chem.* **2011**, *696*, 3807–3815.
20. (a) Gök, Y.; Kantekin, H.; Değirmencioglu, I. *Supramol. Chem.* **2003**, *15*, 335–343; (b) Bilgin, A.; Ertem, B.; Gök, Y. *Eur. J. Inorg. Chem.* **2007**, 1703–1712; (c) Kroenke, W.; Kenney, M. E. *Inorg. Chem* **1964**, *3*, 696–698; (d) Bilgin, A.; Ertem, B.; Gök, Y. *Tetrahedron Lett.* **2003**, *44*, 3829–3833.

21. (a) Wang, C.; Bryce, M. R.; Batsanov, A. S.; Stanley, F. C.; Beeby, A.; Howard, J. A. K. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1671–1678; (b) George, R. D.; Snow, A. W. *Chem. Mater.* **1994**, *6*, 1587–1588; (c) Vacus, J.; Simon, J. *Adv. Mater.* **1995**, *7*, 797–800.
22. Gök, Y.; Kantekin, H.; Bilgin, A.; Mendil, D.; Değirmencioglu, I. *Chem. Commun.* **2001**, 285–286.
23. Çakır, V.; Çakır, D.; Bıyıklıoğlu, Z.; Kantekin, H. *J. Inclusion Phenom. Macrocycl. Chem.* **2012**. http://dx.doi.org/10.1007/s10847-012-0270-1.