Phthalocyanine Synthesis in Ionic Liquids: Preparation of Differently Substituted Phthalocyanines in Tetrabutylammonium Bromide

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Abstract: A series of alkylthio, alkoxy, and phenoxy phthalonitriles have been prepared by nucleophilic substitution reactions on suitable phthalonitrile precursors in molten tetrabutylammonium bromide. This readily available and inexpensive ionic liquid can also be used as a medium for the cyclization of these dinitriles giving the corresponding substituted phthalocyanines.

Key words: phthalonitriles, phthalocyanines, ionic liquids, nucleophilic substitution reactions

Phthalocyanines represent an important class of functional materials.[1] Owing to the many desirable physical and chemical characteristics, these highly conjugated compounds have found practical applications in various disciplines such as molecular opto-electronics,[2] catalysis,[3] and photodynamic therapy,[4] in addition to their traditional use as industrial dyes and pigments.[5] In view of these important applications, there is a need to develop efficient synthetic methods for differently substituted phthalocyanines, in particular those methods which are easy to operate and environmentally benign if one considers the large-scale preparation of these materials. Substituents on the peripheral positions are usually introduced through nucleophilic substitution of common phthalonitrile precursors such as 3- (or 4)-nitrophthalonitrile, 4,5-dichlorophthalonitrile, and 2,3-dicyanohydroquinone.[6] These reactions together with the subsequent cyclization are usually performed in organic solvents. Solid-state syntheses, which can be promoted by microwave irradiation,[7] are not common for substituted phthalocyanines.[8] Recently, ionic liquids have emerged as superior reaction media in organic synthesis because of their low vapor pressure, high thermal stability, high ionic conductivity, and ease of recovery.[9] Although a vast number of reactions can now be performed in these media, to our knowledge, preparation of phthalocyanines in ionic liquids has not been reported so far.[10] We describe herein the use of tetrabutylammonium bromide as a low-cost ionic liquid medium for the preparation of differently substituted phthalonitriles and their corresponding metal-free and metallophthalocyanines.

Owing to the ionic nature, ionic liquids are particularly useful for reactions involving charged reactive species.[9] For nucleophilic substitution reactions, they can enhance the reactivity of the nucleophiles, reducing the yield of the side products formed.[11] On this basis, we extended the present studies using the inexpensive ionic liquid tetrabutylammonium bromide as a reaction medium to prepare a series of substituted phthalonitriles. The preparation was mainly based on nucleophilic aromatic substitution reactions of common nitro-, chloro-, and fluoro-phthalonitrile precursors. We first examined the reactions with thiols, which have a high nucleophilicity. As shown in Table 1, treatment of 4-nitrophthalonitrile (**1a**) with one equivalent of 1-octanethiol or 1-dodecanethiol in one equivalent of tetrabutylammonium bromide at 90 °C gives the corresponding substituted products **2a** and **2b** in ca. 30% yield (Table 1, entries 1 and 3). Addition of two equivalents of thiols and increasing the temperature to 100 °C increase the yield up to 79% (Table 1, entries 2, 4, and 5). 3-Nitrophthalonitrile (**1b**) reacts with these thiols in a similar manner giving the corresponding 3-alkylthiophthalonitriles **2c** and **2d** in excellent yields (Table 1, entries 6 and 7). These reactions can be performed in gram scale with comparable yields and, as expected, the ionic liquid can be recycled (see Experimental Section). Another remarkable feature of these reactions is that base such as K_2CO_3 is not needed. This is in contrast to the analogous reactions performed in organic solvents.[12] It seems that the ionic liquid medium has an additional function to enhance the nucleophilicity of the thiols.[13] Interestingly, when four equivalents of these thiols was used, the reactions with **1a** gave a substantial amount of the metal-free tetrakis(alkylthio)phthalocyanines **3a** (11%) and **3b** (23%) (Scheme 1). Similar reactions with **1b**, however, only led to trace amounts of metal-free phthalocyanines with a substantial amount of substituted phthalonitriles **2c** and **2d** as detected by TLC analysis. Although the role of the excess amounts of thiols in promoting the cyclization of **2a** and **2b** is not clear at this stage, this one-pot synthesis of tetrakis(alkylthio)phthalocyanines from the commercially available 4-nitrophthalonitrile (**1a**) is worth noting.

Apart from the monosubstitution, di- and tetrasubstitution reactions were also performed using 4,5-dichlorophthalonitrile (**1c**) and tetrafluorophthalonitrile (**1d**) as the starting materials. The reactions of these dinitriles with 1-octanethiol gave the desired di- and tetrathiolated dinitriles in moderate yields (Table 1, entries 8 and 9). The reaction of **1c**, however, required the addition of two equivalents of K_2CO_3.

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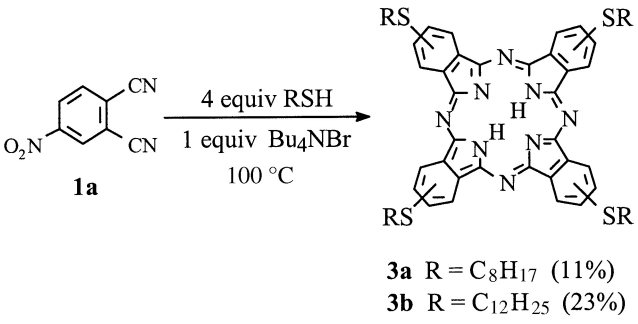
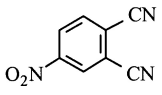
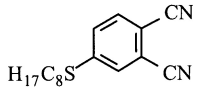
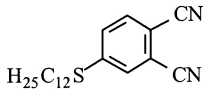
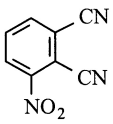
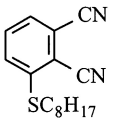
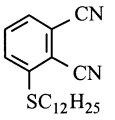
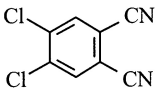
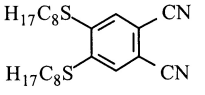
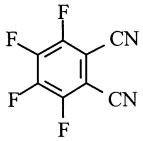
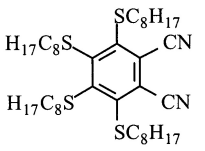


Scheme 1

The nucleophilic aromatic substitution reactions of these phthalonitrile precursors with alcohols could also be performed in tetrabutylammonium bromide in the presence of K_2CO_3. Treatment of 3- or 4-nitrophthalonitrile (**1a** or **1b**) with 1-octanol gave the corresponding octyloxyphthalonitrile **2g** or **2h**, respectively. The yield increased upon addition of a larger amount of 1-octanol and K_2CO_3 (Table 2, entries 1–4). Similarly, treatment of 4,5-dichlorophthalonitrile (**1c**) with phenol and K_2CO_3 in tetrabutylammonium bromide also gave the disubstituted product **2i** in satisfactory yield (Table 2, entry 5). 2,3-Dicyanohydroquinone (**1e**) is a very common precursor for 3,6-dialkoxyphthalonitriles, which can be prepared by typical nucleophilic substitution reactions. As demonstrated by the reaction of **1e** and 1-bromoheptane (Table 2, entry 6), these reactions could also be performed in this ionic liquid effectively.

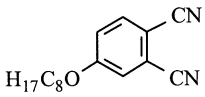
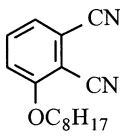
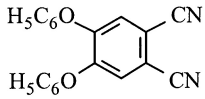
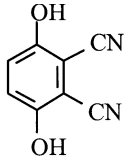
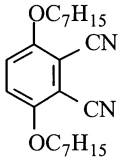
The results summarized in Tables 1 and 2 show that a wide range of substituted phthalonitriles can be prepared in molten tetrabutylammonium bromide. It is worth noting that these nucleophilic substitution reactions are usually performed in dipolar aprotic solvents such as *N*,*N*-dimethylformamide and dimethyl sulfoxide.[12,14] The use

Table 1 Preparation of Alkylthio Phthalonitriles in Tetrabutylammonium Bromide[a]

Entry	Precursor	Thiol	Thiol (equiv)	Temp (°C)	Product	Yield (%)
1	 **1a**	$C_8H_{17}SH$	1	90	 **2a**	29
2	**1a**	$C_8H_{17}SH$	2	100	**2a**	77
3	**1a**	$C_{12}H_{25}SH$	1	90	 **2b**	30
4	**1a**	$C_{12}H_{25}SH$	1	100	**2b**	51
5	**1a**	$C_{12}H_{25}SH$	2	100	**2b**	79
6	 **1b**	$C_8H_{17}SH$	2	100	 **2c**	91
7	**1b**	$C_{12}H_{25}SH$	2	100	 **2d**	93
8[b]	 **1c**	$C_8H_{17}SH$	5	100	 **2e**	50
9	 **1d**	$C_8H_{17}SH$	8	100	 **2f**	55

[a] All reactions were performed in 1 equiv of Bu_4NBr in the absence of K_2CO_3 for 16 h unless otherwise stated.
[b] In the presence of 2 equiv of K_2CO_3.

Table 2 Preparation of Alkoxy and Phenoxy Phthalonitriles in Tetrabutylammonium Bromide[a]

Entry	Precursor	Alcohol/Alkyl Halide	Equiv of Alcohol/ Alkyl Halide	Equiv of K_2CO_3	Product	Yield (%)
1	**1a**	$C_8H_{17}OH$	1.5	6	 **2g**	19
2	**1a**	$C_8H_{17}OH$	4	8	**2g**	39
3	**1b**	$C_8H_{17}OH$	1.5	6	 **2h**	20
4	**1b**	$C_8H_{17}OH$	4	8	**2h**	72
5[b]	**1c**	C_6H_5OH	3	15	 **2i**	39
6[c]	 **1e**	$C_7H_{15}Br$	3	8	 **2j**	86

[a] All reactions were performed in 1 equiv of Bu_4NBr at 100 °C for 24 h unless otherwise stated.
[b] Using 10 equiv of Bu_4NBr.
[c] Using 2 equiv of Bu_4NBr at 120 °C.

of this commercially available ionic liquid, which can be used as received, can greatly simplify the procedure including a prior solvent treatment and subsequent removal of the high-boiling solvents. The solvent-free condition and the recyclable property of the medium make these reactions attractive as an environmentally benign method to prepare these useful phthalocyanine precursors.

With a range of substituted dinitriles, we then examined the feasibility of using this medium to perform their cyclization reactions. As shown in Table 3, treatment of various mono- and disubstituted phthalonitriles with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in molten tetrabutylammonium bromide (130 °C) gives the corresponding metal-free phthalocyanines. The yields are comparable with those obtained in classical organic solvent media.[14b,15] Again, both the set-up and work-up procedures are simplified because of the unique nature of this ionic liquid medium. These reaction conditions, however, could not lead to the formation of desired phthalocyanines from the dinitriles **2i** and **2j**. Some unidentified products were formed in these reactions.

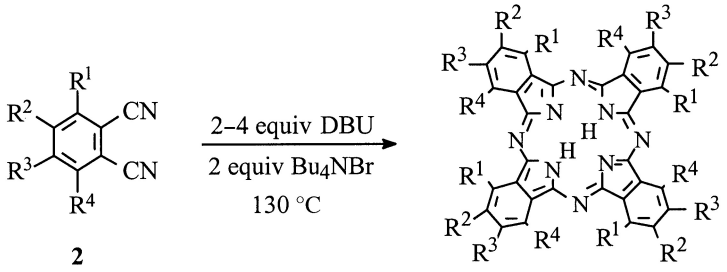
Apart from the metal-free phthalocyanines, metallated derivatives could also be prepared in this medium with the addition of the corresponding metal salts. Several substituted phthalonitriles from Table 1 were chosen arbitrarily to react with DBU and various metal salts including $Zn(OAc)_2 \cdot 2H_2O$, $CoCl_2$, and $Ni(OAc)_2 \cdot 4H_2O$ in molten tetrabutylammonium bromide. The reactions gave the corresponding metallophthalocyanines in moderate yields. The results are summarized in Table 4.

In summary, we have described a convenient and general procedure for the preparation of differently substituted phthalonitriles and the corresponding phthalocyanines. The method employs the inexpensive tetrabutylammonium bromide as the reaction medium instead of the traditional organic solvents.

All reactions were carried out under N_2. Phthalonitriles **1c**,[14b] **2k**,[16] and **2m**[14d] were prepared by literature procedures. Bu_4NBr (98%, Acros) and other reagents were used as received. Virtually all the phthalonitriles **2** and phthalocyanines **3** and **4** reported herein have been described previously either in literature or in patent.[17]

^1H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz) in $CDCl_3$ unless otherwise stated. Spectra were referenced internally by using the residual solvent resonance ($\delta = 7.26$) relative to $SiMe_4$. EI and FAB mass spectra were measured on a Thermo Finnigan MAT 95 XL mass spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra were obtained on a Bruker bench TOF mass spectrometer equipped with a standard UV-laser desorption source, using α-cyano-4-hy-

Table 3 Preparation of Metal-Free Phthalocyanines in Tetrabutylammonium Bromide



2 **3**

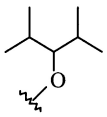
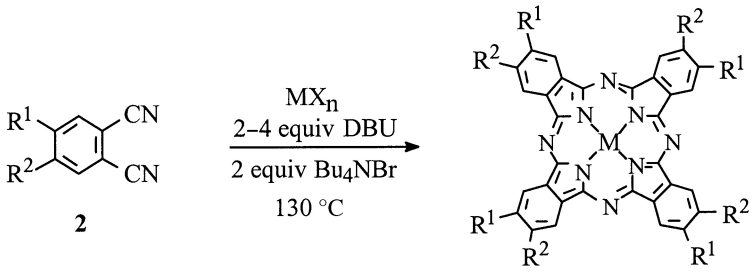
Entry	Phthalonitrile	R^1	R^2	R^3	R^4	Phthalocyanine	Yield (%)
1	**2a**	H	SC_8H_{17}	H	H	**3a**	20
2	**2b**	H	$SC_{12}H_{25}$	H	H	**3b**	20
3	**2c**	SC_8H_{17}	H	H	H	**3c**	13
4	**2k**	H	SC_4H_9	SC_4H_9	H	**3d**	50
5	**2e**	H	SC_8H_{17}	SC_8H_{17}	H	**3e**	50
6	**2g**	H	OC_8H_{17}	H	H	**3f**	20
7	**2m**		H	H	H	**3g**	40

Table 4 Preparation of Metallophthalocyanines in Tetrabutylammonium Bromide



2 **4**

Entry	Phthalonitrile	R^1	R^2	M	Phthalocyanine	Yield (%)
1	**2b**	$SC_{12}H_{25}$	H	Zn	**4a**	31
2	**2k**	SC_4H_9	SC_4H_9	Zn	**4b**	67
3	**2k**	SC_4H_9	SC_4H_9	Co	**4c**	33
4	**2e**	SC_8H_{17}	SC_8H_{17}	Zn	**4d**	20
5	**2e**	SC_8H_{17}	SC_8H_{17}	Ni	**4e**	50

droxycinnamic acid as matrix. UV-Vis spectra were taken on a Cary 5G UV-Vis-NIR spectrophotometer.

Phthalonitriles 2; General Procedure

According to the conditions described in Tables 1 and 2, phthalonitriles **1a–e** (500 mg) were treated with thiols, alcohols, or 1-bromoheptane (and K_2CO_3) in molten Bu_4NBr. After cooling, the mixtures were extracted with Et_2O (3 × 25 mL) and the ionic liquid could be recovered by filtration and re-used after washing extensively with Et_2O. The combined Et_2O extracts were rotary-evaporated and the crude products were purified either by column chromatography or recrystallization. A larger quantity of **1b** (1 g) reacted with 1-octanethiol giving **2c** in 82% yield, while **1c** (1 g) reacted with phenol affording **2i** in 37% yield.

4-Octylthiophthalonitrile (2a)[12b]
^{1}H NMR: δ = 7.63 (d, *J* = 8.4 Hz, 1 H, ArH), 7.54 (d, *J* = 1.8 Hz, 1 H, ArH), 7.48 (dd, *J* = 1.8, 8.4 Hz, 1 H, ArH), 3.00 (t, *J* = 7.2 Hz, 2 H, SCH_2), 1.72 (quintet, *J* = 7.2 Hz, 2 H, CH_2), 1.40–1.52 (m, 2 H, CH_2), 1.26–1.38 (m, 8 H, CH_2), 0.89 (t, *J* = 6.9 Hz, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 272 (21, [M$^+$]), 178 (44), 145 (39), 91 (51), 71 (86), 57 (100).

HRMS (EI): *m*/*z* calcd for $C_{16}H_{20}N_2S$: 272.1342; found: 272.1341.

4-Dodecylthiophthalonitrile (2b)[12a]
^{1}H NMR: δ = 7.63 (d, *J* = 8.4 Hz, 1 H, ArH), 7.54 (d, *J* = 2.1 Hz, 1 H, ArH), 7.48 (dd, *J* = 2.1, 8.4 Hz, 1 H, ArH), 3.00 (t, *J* = 7.5 Hz, 2 H, SCH_2), 1.71 (quintet, *J* = 7.5 Hz, 2 H, CH_2), 1.40–1.48 (m, 2 H, CH_2), 1.21–1.35 (m, 16 H, CH_2), 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 328 (91, [M$^+$]), 149 (71), 69 (82), 57 (100).

HRMS (EI): *m*/*z* calcd for $C_{20}H_{28}N_2S$: 328.1968; found: 328.1961.

3-Octylthiophthalonitrile (2c)[17c]
^{1}H NMR: δ = 7.52–7.63 (m, 3 H, ArH), 3.05 (t, *J* = 7.5 Hz, 2 H, SCH_2), 1.71 (quintet, *J* = 7.5 Hz, 2 H, CH_2), 1.41–1.50 (m, 2 H, CH_2), 1.22–1.32 (m, 8 H, CH_2), 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3).

MS (EI): *m*/*z* = 272 (33, [M$^+$]), 160 (79), 71 (83), 57 (100).

HRMS (EI): *m*/*z* calcd for $C_{16}H_{20}N_2S$: 272.1342; found: 272.1337.

3-Dodecylthiophthalonitrile (2d)[17d]
^{1}H NMR: δ = 7.52–7.60 (m, 3 H, ArH), 3.05 (t, *J* = 7.2 Hz, 2 H, SCH_2), 1.71 (quintet, *J* = 7.2 Hz, 2 H, CH_2), 1.41–1.50 (m, 2 H, CH_2), 1.20–1.32 (m, 16 H, CH_2), 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 328 (31, [M$^+$]), 149 (79), 69 (77), 57 (100).

HRMS (EI): *m*/*z* calcd for $C_{20}H_{28}N_2S$: 328.1968; found: 328.1970.

4,5-Bis(octylthio)phthalonitrile (2e)[12b]
^{1}H NMR: δ = 7.40 (s, 2 H, ArH), 3.00 (t, *J* = 7.5 Hz, 4 H, SCH_2), 1.74 (quintet, *J* = 7.5 Hz, 4 H, CH_2), 1.41–1.52 (m, 4 H, CH_2), 1.23–1.34 (m, 16 H, CH_2), 0.88 (t, *J* = 7.2 Hz, 6 H, CH_3).

MS (EI): *m*/*z* (%) = 416 (22, [M$^+$]), 304 (37), 149 (62), 69 (100).

HRMS (EI): *m*/*z* calcd for $C_{24}H_{36}N_2S_2$: 416.2314; found: 416.2311.

Tetrakis(octylthio)phthalonitrile (2f)[17e]
^{1}H NMR: δ = 3.07 (t, *J* = 7.5 Hz, 4 H, SCH_2), 3.02 (t, *J* = 7.5 Hz, 4 H, SCH_2), 1.20–1.60 (m, 48 H, CH_2), 0.86 (t, *J* = 6.6 Hz, 12 H, CH_3).

4-Octyloxyphthalonitrile (2g)[17f]
^{1}H NMR: δ = 7.70 (d, *J* = 8.7 Hz, 1 H, ArH), 7.25 (d, *J* = 2.4 Hz, 1 H, ArH), 7.17 (dd, *J* = 2.4, 8.7 Hz, 1 H, ArH), 4.04 (t, *J* = 6.6 Hz, 2 H, OCH_2), 1.82 (quintet, *J* = 6.6 Hz, 2 H, CH_2), 1.38–1.48 (m, 2 H, CH_2), 1.24–1.36 (m, 8 H, CH_2), 0.90 (t, *J* = 6.9 Hz, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 256 (23, [M$^+$]), 71 (88), 57 (100).

HRMS (EI): *m*/*z* calcd for $C_{16}H_{20}N_2O$: 256.1570; found: 256.1572.

3-Octyloxyphthalonitrile (2h)
^{1}H NMR: δ = 7.65 (t, *J* = 8.1 Hz, 1 H, ArH), 7.33 (d, *J* = 8.1 Hz, 1 H, ArH), 7.25 (d, *J* = 8.1 Hz, 1 H, ArH), 4.14 (t, *J* = 6.6 Hz, 2 H, OCH_2), 1.87 (quintet, *J* = 6.6 Hz, 2 H, CH_2), 1.43–1.54 (m, 2 H, CH_2), 1.24–1.38 (m, 8 H, CH_2), 0.89 (t, *J* = 6.9 Hz, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 256 (18, [M$^+$]), 227 (32), 71 (90), 57 (100).

HRMS (EI): *m*/*z* calcd for $C_{16}H_{20}N_2O$: 256.1570; found: 256.1573.

4,5-Bis(phenyloxy)phthalonitrile (2i)[14b]
^{1}H NMR: δ = 7.35 (t, *J* = 7.5 Hz, 4 H, ArH), 7.19 (s, 2 H, ArH), 7.16 (t, *J* = 7.5 Hz, 2 H, ArH), 7.02 (d, *J* = 7.5 Hz, 4 H, ArH).

MS (EI): *m*/*z* (%) = 331 (100), 312 (16, [M$^+$]), 195 (41), 77 (39).

3,6-Bis(heptyloxy)phthalonitrile (2j)[17h]
^{1}H NMR: δ = 7.14 (s, 2 H, ArH), 4.04 (t, *J* = 6.3 Hz, 4 H, OCH_2), 1.82 (quintet, *J* = 6.3 Hz, 4 H, CH_2), 1.40–1.50 (m, 4 H, CH_2), 1.26–1.36 (m, 12 H, CH_2), 0.89 (t, *J* = 6.9 Hz, 6 H, CH_3).

MS (EI): *m*/*z* (%) = 356 (8, [M$^+$]), 160 (92), 98 (83), 57 (100).

HRMS (EI): *m*/*z* calcd for $C_{22}H_{32}N_2O_2$: 356.2458; found: 356.2451.

Phthalocyanines 3 and 4; General Procedure
A mixture of phthalonitrile **2** (100 mg) [and MX_n (0.4 equiv) (for the preparation of **4**)] in Bu_4NBr (2 equiv) was heated to 90 °C, then a few drops of DBU (2–4 equiv) were added. The mixture was heated overnight at 130 °C to give a deep green solution. After a brief cooling, the mixture was mixed with EtOH–H_2O (1:1, 20 mL) and filtered. The crude product was then purified by column chromatography. The nickel phthalocyanine **4e** was unstable in EtOH–H_2O. The reaction mixture was loaded directly onto a silica gel column for purification (Tables 3 and 4).

2(3),9(10),16(17),23(24)-Tetrakis(octylthio)phthalocyanine (3a)[17i]
^{1}H NMR: δ = 6.93–7.57 (m, 12 H, PcH), 3.04–3.23 (m, 8 H, SCH_2), 1.89–1.98 (m, 8 H, CH_2), 1.60–1.72 (m, 8 H, CH_2), 1.35–1.52 (m, 32 H, CH_2), 0.98–1.02 (m, 12 H, CH_3), –6.37 (br s, 2 H, NH).

MS (MALDI-TOF): an isotopic cluster peaking at *m*/*z* = 1090.17 (calcd for M$^+$: 1090.55).

UV-Vis ($CHCl_3$): λ_{max} = 337, 602, 633, 663, 699 nm.

2(3),9(10),16(17),23(24)-Tetrakis(dodecylthio)phthalocyanine (3b)[12a]
^{1}H NMR: δ = 7.21–7.90 (m, 12 H, PcH), 3.18–3.34 (m, 8 H, SCH_2), 1.92–2.10 (m, 8 H, CH_2), 1.68–1.86 (m, 8 H, CH_2), 1.20–1.54 (m, 64 H, CH_2), 0.82–0.96 (m, 12 H, CH_3).

MS (MALDI-TOF): an isotopic cluster peaking at *m*/*z* = 1314.42 (calcd for M$^+$: 1314.80).

UV-Vis ($CHCl_3$): λ_{max} = 344, 425, 617, 648, 683, 715 nm.

1(4),8(11),15(18),22(25)-Tetrakis(octylthio)phthalocyanine (3c)[17c]
^{1}H NMR: δ = 8.10–8.55 (m, 4 H, PcH), 6.98–7.58 (m, 8 H, PcH), 2.66–3.36 (m, 8 H, SCH_2), 1.22–2.18 (m, 48 H, CH_2), 0.82–1.02 (m, 12 H, CH_3), –2.47 to –2.35 (m, 2 H, NH).

MS (MALDI-TOF): an isotopic cluster peaking at *m*/*z* = 1090.22 (calcd for M$^+$: 1090.55).

UV-Vis ($CHCl_3$): λ_{max} = 334, 420 (sh), 638, 665, 702, 732 nm.

2,3,9,10,16,17,23,24-Octakis(butylthio)phthalocyanine (3d)[17j]
^{1}H NMR: δ = 8.48 (s, 8 H, PcH), 3.42 (t, *J* = 7.5 Hz, 16 H, SCH_2), 2.06 (quintet, *J* = 7.5 Hz, 16 H, CH_2), 1.79 (sextet, *J* = 7.5 Hz, 16 H, CH_2), 1.20 (t, *J* = 7.5 Hz, 24 H, CH_3).

MS (MALDI-TOF): an isotopic cluster peaking at *m*/*z* = 1218.24 (calcd for M$^+$: 1218.44).

UV-Vis ($CHCl_3$): λ_{max} = 323, 360, 447, 635, 668, 700, 733 nm.

2,3,9,10,16,17,23,24-Octakis(octylthio)phthalocyanine (3e)[17k]
^{1}H NMR: δ = 8.46 (br s, 8 H, PcH), 3.43 (br s, 16 H, SCH_2), 2.08 (br s, 16 H, CH_2), 1.78 (br s, 16 H, CH_2), 1.28–1.56 (m, 64 H, CH_2), 0.91 (br s, 24 H, CH_3).

MS (MALDI-TOF): an isotopic cluster peaking at *m*/*z* = 1667.63 (calcd for M$^+$: 1666.94).

UV-Vis ($CHCl_3$): λ_{max} = 323, 430 (sh), 635, 668, 700, 732 nm.

2(3),9(10),16(17),23(24)-Tetrakis(octyloxy)phthalocyanine (3f)[17l]

^{1}H NMR: δ = 6.73–8.90 (m, 12 H, PcH), 3.78–4.10 (m, 8 H, OCH_2), 1.88–2.08 (m, 8 H, CH_2), 0.88–1.77 (m, 52 H, CH_2 and CH_3), –5.24 (br s, 2 H, NH).

MS (FAB): *m*/*z* = 1026 (7, [M^+]), 970 (8), 914 (7), 307 (46), 154 (100), 137 (64).

HRMS (FAB): *m*/*z* calcd for $C_{64}H_{82}N_8O_4$: 1026.6454; found: 1026.6419.

UV-Vis ($CHCl_3$): λ_{max} = 341, 390, 610, 646, 669, 706 nm.

1(4),8(11),15(18),22(25)-Tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyanine (3g)[15c]

^{1}H NMR: δ = 9.04–9.12 (m, 4 H, PcH), 8.03–8.10 (m, 4 H, PcH), 7.66–7.74 (m, 4 H, PcH), 4.31–4.72 (m, 4 H, OCH), 2.30–2.66 (m, 8 H, CH), 1.49–1.54 (m, 24 H, CH_3), 1.21–1.26 (m, 24 H, CH_3), –0.06 to 0.09 (m, 2 H, NH).

MS (MALDI-TOF): an isotopic cluster peaking at *m*/*z* = 970.61 (calcd for M^+: 970.58).

UV-Vis ($CHCl_3$): λ_{max} = 318, 632, 667, 700, 731 nm.

[2(3),9(10),16(17),23(24)-Tetrakis(dodecylthio)phthalocyaninato]zinc(II) (4a)

^{1}H NMR: δ = 6.70–7.75 (m, 12 H, PcH), 2.40–2.90 (m, 8 H, SCH_2), 1.20–1.60 (m, 80 H, CH_2), 0.88–0.92 (m, 12 H, CH_3).

MS (MALDI-TOF): an isotopic cluster starting at *m*/*z* = 1376.35 (calcd for M^+: 1376.72).

UV-Vis ($CHCl_3$): λ_{max} = 357, 625, 662, 693 nm.

[2,3,9,10,16,17,23,24-Octakis(butylthio)phthalocyaninato]zinc(II) (4b)[16]

^{1}H NMR (pyridine-d_5): δ = 9.35 (s, 8 H, PcH), 3.60 (t, *J* = 7.2 Hz, 16 H, SCH_2), 2.06 (quintet, *J* = 7.2 Hz, 16 H, CH_2), 1.77 (sextet, *J* = 7.2 Hz, 16 H, CH_2), 1.10 (t, *J* = 7.2 Hz, 24 H, CH_3).

MS (MALDI-TOF): an isotopic cluster starting at *m*/*z* = 1280.29 (calcd for M^+: 1280.36).

UV-Vis (THF): λ_{max} = 366, 626, 695 nm.

[2,3,9,10,16,17,23,24-Octakis(butylthio)phthalocyaninato]cobalt(II) (4c)[17o]

MS (FAB): *m*/*z* (%) = 1276 (3, [M^+]), 154 (66), 69 (74), 55 (100).

UV-Vis (THF): λ_{max} = 334, 616, 680 nm.

[2,3,9,10,16,17,23,24-Octakis(octylthio)phthalocyaninato]zinc(II) (4d)[17k]

^{1}H NMR: δ = 8.12 (br s, 8 H, PcH), 3.04 (br s, 16 H, SCH_2), 1.79 (br s, 16 H, CH_2), 1.25–1.61 (m, 80 H, CH_2), 0.91 (br s, 24 H, CH_3).

MS (MALDI-TOF): an isotopic cluster starting at *m*/*z* = 1728.66 (calcd for M^+: 1728.86).

UV-Vis ($CHCl_3$): λ_{max} = 368, 638, 702 nm.

[2,3,9,10,16,17,23,24-Octakis(octylthio)phthalocyaninato]nickel(II) (4e)[17p]

^{1}H NMR: δ = 8.30 (br s, 8 H, PcH), 3.38 (br s, 16 H, SCH_2), 2.04 (br s, 16 H, CH_2), 1.74 (br s, 16 H, CH_2), 1.20–1.58 (m, 64 H, CH_2), 0.90 (br s, 24 H, CH_3).

MS (MALDI-TOF): an isotopic cluster starting at *m*/*z* = 1722.22 (calcd for M^+: 1722.86).

UV-Vis (THF): λ_{max} = 319, 432, 635, 670, 702 nm.

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