Dyes and Pigments **18** (1992) 91–102

Efficient Synthesis of Phthalocyanines and Related Macrocyclic Compounds in the Presence of Organic Bases

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(Received 14 July 1991; accepted 6 August 1991)

ABSTRACT

Various unsubstituted and substituted aromatic 1,2-dinitriles were converted in the presence of strong bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in bulk reactions or an n-pentanol in high yields to metal-free phthalocyanines and related macrocyclic compounds. These efficient pathways, using commercially available bases, are easy to perform and work under relatively mild conditions. Bases weaker than DBU or DBN result in lower yield of phthalocyanines or impure products. Reactions in the presence of metal salts lead to metal phthalocyanines in yields similar to the metal-free analogues.

1 INTRODUCTION

Unsubstituted and substituted phthalocyanines are widely used as dyes and pigments. In addition, various other properties showing new applications have been investigated in recent years:[1–8] photosensitization in solution, photodynamic activity in photodynamic cancer therapy, electrocatalysts for the dioxygen reduction in fuel-cell reactions, photoreductions or photooxidations in photoelectrochemical cells, electrochromic processes as thin films, charge separation in photovoltaic cells, electrophotographic applications, optical information-storage systems, catalysts for mercaptan oxidations, and use as sensors. For most of these applications, phthalocyanines bearing

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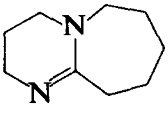
Dyes and Pigments 0143-7208/92/$05.00 © 1992 Elsevier Science Publishers Ltd, England. Printed in Great Britain

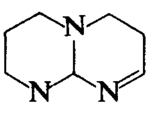
special substituents were prepared in order to enhance their solubility or to influence the electron density of the interior ligand.

A convenient high-yield synthesis is a fundamental prerequisite for new applications. Most synthetic procedures for metal-free phthalocyanines give low yields and need to be improved. Most pure phthalocyanines are prepared by the cyclotetramerization reactions of aromatic 1,2-dicyano benzenes and 1,3-diiminoisoindolenines.[1,2] Refluxing phthalonitriles with sodium or lithium n-pentoxide in n-pentanol or other alcohols results in alkali-containing phthalocyanines, which can be demetallized with conc. sulfuric acid. Similarly, the reaction product of the dinitrile with Na or Mg at 200°C needs to be demetallized with conc. sulfuric acid. The reaction of phthalonitriles in 2-*N*,*N*-dimethylaminoethanol under reflux requires ammonia gas for direct formation of the metal-free phthalocyanine. Yields for unsubstituted compounds are high but are often low for substituted derivatives. A good alternative method consists of two steps, the initial formation of 1,3-diiminoisoindolenines by using ammonia in a low-boiling alcohol followed by their tetramerization to phthalocyanines in high yield in refluxing 2-*N*,*N*-dimethylaminoethanol, even for some substituted derivatives.

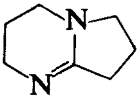
In 1980 and 1983, Tomada *et al.*[9,10] published a simple synthesis of phthalocyanines by reacting 1,2-dicyanobenzene in alcohols with 1,5-diazabicyclo[4.3.0]non-5-en (DBN) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as strong bases. Yields up to 70% for metal-free and 80% for metal-containing phthalocyanines were achieved. We have used this method for the preparation of various substituted phthalocyanines and related macrocyclic compounds. With respect to the importance of this procedure, we report our experiments. Various dinitriles were reacted in the presence of DBN, DBU, or other bases, such as 2-*N*,*N*-dimethylaminoethanol (DMAE), 1,2,3,6-tetrahydropyridine (THP), triethylamine (TEA), pyridine (Py),



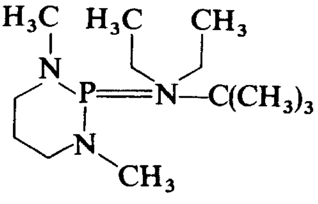
DBU



TBD



DBN

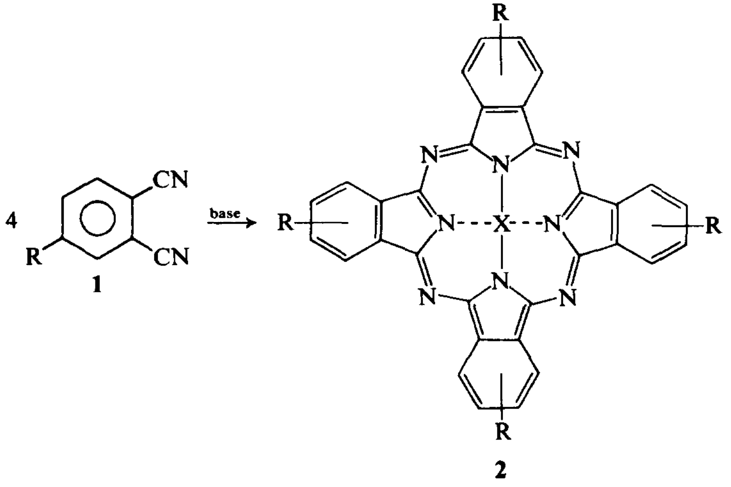


BEMP

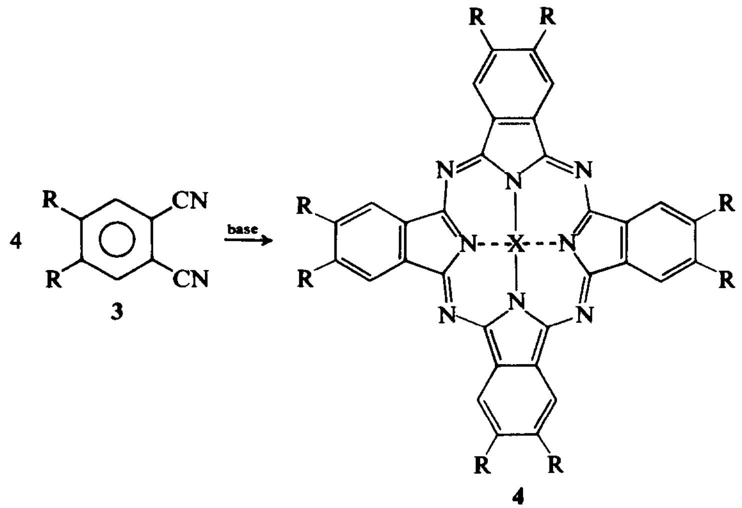
triphenylphosphine (TPP), 1,5,7-triazabicyclo[4.4.0]dec-5-en (TBD), and 2-tert.-butylimino-2-diethylamino-1,3-dimethylperhydrodiazophosphorin (BEMP) in bulk or in a high-boiling alcohol.

2 RESULTS

On heating the dinitriles **1a, c–i** with DBN (DBU led to similar results) in a sealed ampoule nearly quantitative yields (80–95%) of pure metal-free phthalocyanines **2a, c–i** were obtained. This is the highest yield of metal-free compounds reported so far. In refluxing n-pentanol in the presence of DBU or DBN, yields of metal-free **2a–d, 4a, b, 6, 8, 10** were 40–90%. In the absence of a base, little or no phthalocyanine is observed. Purity of the products was

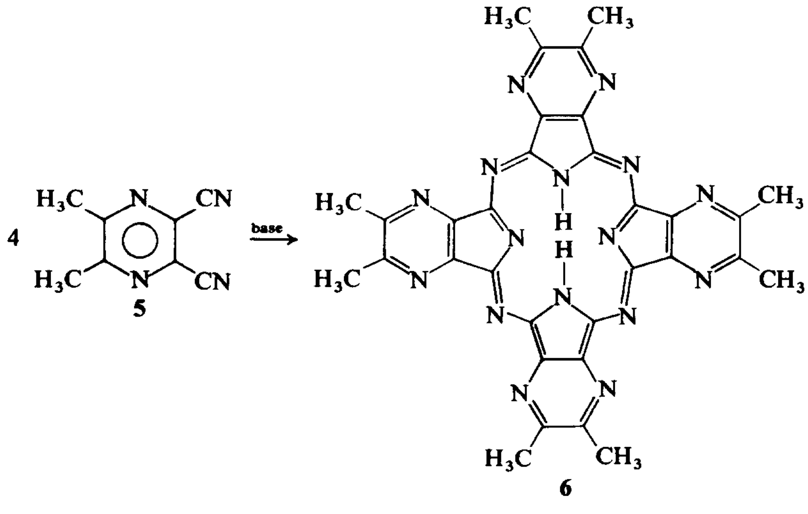


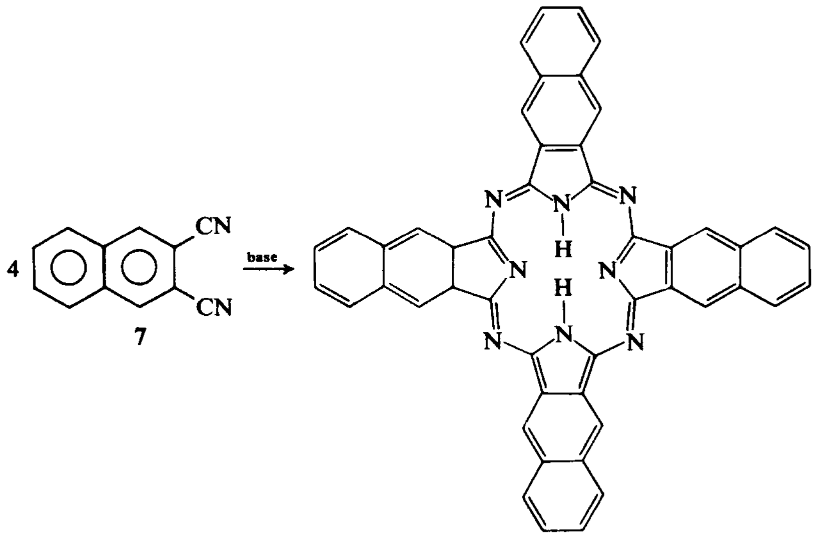
	R
1a, 2a (X = 2H, Cu, Co, Ni, Pb)	—H
1b, 2b (X = 2H)	—NO_2
1c, 2c (X = 2H)	—O—C_6H_5
1d, 2d (X = 2H)	—O—C_6H_4(p)—$C(CH_3)_3$
1e, 2e (X = 2H)	—O—C_6H_4(p)—NO_2
1f, 2f (X = 2H)	—O—C_6H_4(p)—OCH_3
1g, 2g (X = 2H)	—O—Py(m)
1h, 2h (X = 2H)	—S—C_6H_5
1i, 2i (X = 2H)	—OCH_3
1j, 2j (X = 2H)	—OCH_2CH_3
1k, 2k (X = 2H)	—$OCH_2CH_2CH_3$
1l	—OH
1m	—NH_2



	R
(**3a**, **4a** (X = 2H)	—OCH_3
3b, **4b** (X = 2H, Cu, Co, Pb, Zn, Sn)	—$OCH_2CH_2CH_2CH_3$

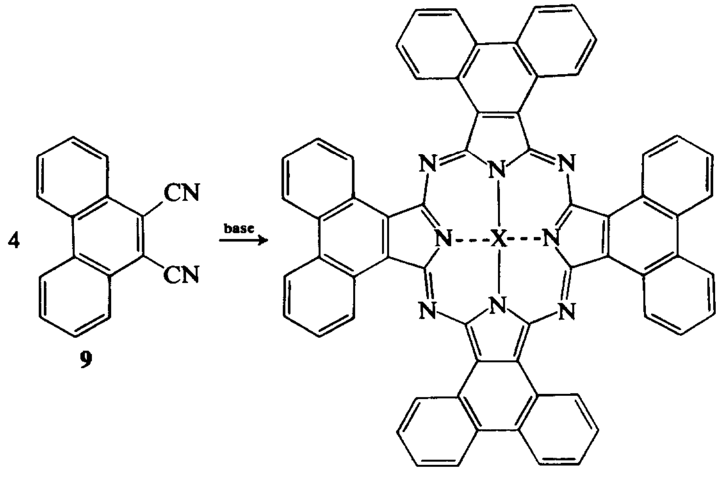
assessed by thin-layer chromatography (TLC), IR- and electronic spectra. TLC showed no soluble reaction products other than the phthalocyanine. In UV–VIS spectra, the characteristic Q-band transition of metal-free phthalocyanines with D_{2h}-symmetry is observed with high intensity.[1] The conversion of the nitrile to the macrocycle can be accompanied by side reactions. IR spectra gave no indication of the formation of triazine





7 **8**

($1520\,cm^{-1}$ and $1360\,cm^{-1}$) and linear C–N chains such as polyisoindolenines (broad absorption at 1620 and $1080\,cm^{-1}$).[11–13] Because phenyl-substituted triazines absorb in the UV region at approximately 230 nm and polyisoindolenines at <500 nm, the intensity ratio of the absorptions at approximately 700:500–230 nm characterizes the purity. This is noted in Tables 1 and 2 as product quality: '+' means an intensity ratio >1, '=' 1–0·5, '−' <0·5. The IR spectra exhibit typical absorptions of the substituents, e.g. $-NO_2$ in **2b** at 1341 and $1522\,cm^{-1}$, $-O-C_{arom}$ in **2c–g** at around $1250\,cm^{-1}$, $-O-C_{alip}$ in **2i–2k**, **4a**, **b** at about $1290–1050\,cm^{-1}$,



9

10
(X = 2H, Cu)

TABLE 1

Results of the Reactions of Substituted 1,2-Dicyanobenzenes with Various Bases in Bulk

Nitrile	*Product*	*Reaction conditions*				*Yield (%)*	*Product quality*[a]
		Coreactant	*Conc. (mol.%)*	*Temp. (°C)*	*Time (h)*		
1a	**2a**	DBN	25	200	4	90	+
1a	**2a**	DBU	25	200	4	82	+
1a	**2a**	DBN	100	200	4	73	+
1a	**2a**	DBU	100	200	4	64	+
1a	**2a**	THP	25	200	4	65	+
1a	**2a**	DMAE	25	200	4	24	+
1b	**2b**	DBN	25	150	4	77	−
1b	**2b**	DBN	25	200	4	95	−
1b	**2b**	THP	25	200	4	85	−
1b	**2b**	DMAE	25	200	4	64	−
1b	**2b**	TPP	25	[b]	[b]	67	−
1c	**2c**	DBN	25	150	4	77	+
1d	**2d**	DBN	12·5	150	2	—	−
1d	**2d**	DBN	12·5	150	4	16	+
1d	**2d**	DBN	12·5	150	8	69	+
1d	**2d**	DBN	12·5	150	24	87	+
1d	**2d**	DBN	25	150	2	—	+
1d	**2d**	DBN	25	150	3	39	+
1d	**2d**	DBN	25	150	4	79	+
1d	**2d**	DBN	25	150	8	85	+
1d	**2d**	DBN	25	150	24	83	+
1d	**2d**	DBN	50	150	2	28	+
1d	**2d**	DBN	50	150	3	75	+
1d	**2d**	DBN	50	150	4	80	+
1d	**2d**	DBN	50	150	8	86	+
1d	**2d**	DBN	50	150	24	90	+
1d	**2d**	DBN	25	175	1	75	+
1d	**2d**	DBN	25	175	2	85	+
1d	**2d**	DBN	25	175	4	95	+
1d	**2d**	DBN	25	200	1	82	+
1d	**2d**	DBN	25	200	2	90	+
1d	**2d**	DBN	25	200	4	85	+
1d	**2d**	DBN	25	200	4	71	+
1d	**2d**	DBN	25	150	4	5	+
1e	**2e**	DBN	25	200	4	87	+
1e	**2e**	THP	25	200	4	86	+
1e	**2e**	TEA	25	150	4	43	+
1e	**2e**	DMAE	25	200	4	80	+
1e	**2e**	TPP	25	[b]	[b]	63	−
1f	**2f**	DBN	25	200	4	92	+
1g	**2g**	DBN	25	150	4	95	+

TABLE 1—*cont.*

Nitrile	*Product*	*Reaction conditions*				*Yield* (%)	*Product quality*[a]
		Coreactant	*Conc.* (*mol.*%)	*Temp.* (°*C*)	*Time* (*h*)		
1g	**2g**	DBN	25	200	4	90	+
1g	**2g**	THP	25	200	4	85	+
1g	**2g**	TAE	25	150	4	2	+
1g	**2g**	DMAE	25	200	4	20	+
1g	**2g**	TPP	25	[b]	[b]	77	−
1h	**2h**	DBN	25	150	4	93	+
1h	**2h**	DBN	25	200	4	96	+
1h	**2h**	THP	25	200	4	90	+
1h	**2h**	TAE	25	150	4	17	+
1h	**2h**	TAE	25	200	4	42	+
1h	**2h**	DMAE	25	200	4	69	+
1h	**2h**	Py	25	200	4	10	+
1h	**2h**	Py	25	250	4	14	+
1i	**2i**	DBN	25	150	4	5	+
1i	**2i**	DBN	25	200	4	87	+
1i	**2i**	THP	25	200	4	82	+
1j	**2j**	DBN	25	150	4	70	+
1k	**2k**	DBN	25	150	4	67	+
1l[c]							
1m[c]							

[a] See test.

[b] Since the reaction mixture had not solidified after 4 h at 200°C, it was heated another 2·5 h at 300°C, after which the given results were obtained.

[c] Very impure products were obtained under various reaction conditions.

$-S-C_{arom}$ in **1h** at 560–700 cm^{-1}. IR- and UV–VIS-spectra of **6**, **8**, and **10** agree with the porphyrin structure and reported values of these compounds.[11,13] ^{1}H-NMR spectra of soluble compounds show typical absorptions for the substituents.

Table 1 shows that the bulk reactions with DBN at 150°C and reaction times of >4 h result in high yields of phthalocyanine (s. especially **1d**). Amounts of >25 mol.% DBN give excellent conversion of the nitriles. Some dinitriles were reacted with DBU in the presence of $CuCl_2$ or $NiCl_2$ (molar ratio nitrile: metal salt—4:1). According to the electronic spectra metal phthalocyanines are formed in a yield and purity comparable with the reactions without metal salts.

Reactions in solution with alcohols of a lower boiling point than n-pentanol, e.g. ethanol, propanol, butanol, gave lower yields. The yield of **2a** from **1a** in ethanol with DBU is about 45% and with DBN about 20% after

TABLE 2

Results of the Reactions of Substituted Dinitriles with Various Bases in n-Pentanol under Reflux (Molar Ratio Dinitrile: Base = 1:1, Reaction Time 36 h)

Nitrile	*Metal salt*	*Product*	*Coreactant*	*Yield* (%)	*Product quality*[a]
1a	—	**2a**	DBN	88	+
1a	—	**2a**	DBU	72	+
1a	—	**2a**	TBD	68	+
1a	—	**2a**	BEMP	59	+
1a	—	—	THP	0	
1a	—	**2a**	DMAE	32	+
1a	—	—	TEA	0	
1a	—	—	Py	0	
1a	$CuCl_2$	**2a**, Cu	DBU	91	+
1a	$CuCl_2$	**2a**, Cu	TBD	43	+
1a	$CuCl_2$	**2a**, Cu	BEMP	92	+
1a	$CoCl_2$	**2a**, Co	DBU	76	+
1a	$CoCl_2$	**2a**, Co	TBD	84	+
1a	$CoCl_2$	**2a**, Co	BEMP	70	+
1a	$NiCl_2$	**2a**, Ni	DBU	91	+
1a	$NiCl_2$	**2a**, Ni	TBD	71	+
1a	$NiCl_2$	**2a**, Ni	BEMP	81	+
1a	$PbCl_2$	**2a**, Pb	DBU	69	+
1a	$PbCl_2$	**2a**, Pb	TBD	83	+
1a	$PbCl_2$	**2a**, Pb	BEMP	64	+
1b	—	**2b**	DBU	64	+
1c	—	**2c**	DBU	45	+
1d	—	**2d**	DBU	38	+
3a	—	**4a**	DBU	40	+
3b	—	**4b**	DBU	37	+
3b	—	**4b**	DBU[b]	24	+
3b	$CuCl_2$	**4b**, Cu	DBU	42	+
3b	$CoCl_2$	**4b**, Co	DBU	38	+
3b	$PbCl_2$	**4b**, Pb	DBU	66	+
3b	$ZnCl_2$	**4b**, Zn	DBU	40	+
3b	Mnacac[c]	**4b**, Mn	DBU	44	−
3b	$SnCl_2$	**4b**, Sn	DBU	6	+
5	—	**6**	DBU	65	+
7	—	**8**	DBU	61	+
9	—	**10**	DBU	46	+
9	$CuCl_2$	**10**, Cu	DBU	68	+

[a] See text.

[b] Molar ratio: dinitrile:base = 4:1.

[c] Mnacac: manganese(II)acetylacetonate.

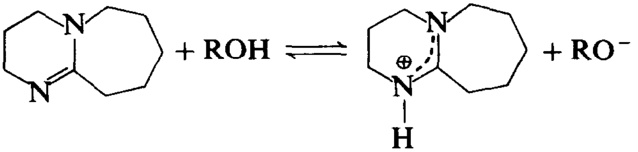
a reaction time of 18 h (molar ratio dinitrile:base—1:1).[1,10] In n-pentanol, reaction times >24 h and a molar ratio of dinitrile:base ~1:1 are necessary for high yields of phthalocyanines **2**. In the presence of metal salts, yields of metal-containing macrocycles are not increased as compared with metal-free ones (Table 2).

The mixture of the base employed for the conversion of the dinitriles has a significant influence on the yields. In bulk reactions, the yields decrease as follows: DBN/DBU > THP > DMAE > TEA > Py (Table 1). Triphenylphosphine results in a high yield of very impure compounds. In refluxing n-pentanol, DBN or DBU give phthalocyanines in high yields and DMAE affords only low yields (Table 2). In the presence of the strong bases TBD and BEMP the formation of phthalocyanine is observed in high yield.

3 DISCUSSION

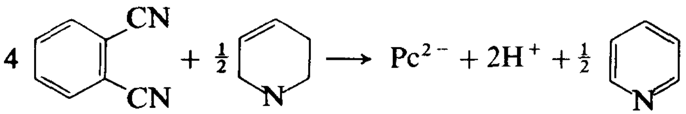
The reaction of various dinitriles in the presence of commercially available DBU/DBN is an excellent procedure for the preparation of metal-free phthalocyanines in very high yields. In addition, metal-containing phthalocyanines can be prepared in comparable yields. The described methods are preferable to others described in the literature. Bulk reactions give higher yields when employing substituted nitriles, but reactions in solutions are easier to perform.

The mechanisms of the reactions in bulk or solution seem to be different. For the reactions in boiling ethanol, Tomada *et al.*[9] proposed the function of the strong bases DBN or DBU as being that of an electron acceptor:



Afterwards, the alkoxide anion adds to a cyano group of a dinitrile with formation of an alkoxyisoindolenine, which in turn reacts, under ring closure-condensation, and oxidation of an equimolar amount of alcohol to aldehyde, to the metal-free phthalocyanine.[1,14] Thus it is expected that, with decreasing pK_b-values of the bases, the amount of free-alkoxide anion increases in equilibrium with DBN or DBU. Strong bases such as DBU ($pK_b = 2{\cdot}5$) promote phthalocyanine formation, whereas weaker bases, such as pyridine ($pK_b = 8{\cdot}7$), TEA ($pK_b = 3{\cdot}3$), and THP do not. In comparison with DBU or DBN, the slightly stronger bases TBD and BEMP[15] did not improve phthalocyanine formation.

In bulk reactions, the yields of metal-free phthalocyanines also increase with increasing pK_b-values (pK_b of THP is not known; in DMAE the electron-attracting OH-group may lower the pK_b-value in comparison with TEA). However, the situation is more complex than in solution. In addition to their nucleophilic character for activating a nitrile group, these compounds also act as proton and electron donor. In the reaction of dinitriles with THP as coreactant, pyridine is observed:[11]



For the other bases used in this work the mechanisms are unknown.

4 EXPERIMENTAL

4.1 General

Electronic spectra were recorded on a Perkin–Elmer 554 or Lambda 9, FT–IR spectra on a Nicolet 5 DX, mass spectra (of dicyano compounds at 70 eV) on a Varian CH 7A and H-NMR spectra (for soluble phthalocyanines) on a Bruker WH 360. All bases, **1a** and other chemicals were obtained in the highest available purity from Merck or Aldrich. n-Pentanol was distilled and dried prior to use.

4.2 Syntheses

The following dinitriles were prepared according to the literature: 4-nitrophthalonitrile (**1b**),[16] 4-hydroxyphthalonitrile (**1l**),[16] 4-aminophthalonitrile (**1m**),[17] 4,5-methoxyphthalonitrile (**3a**),[18] 4,5-dibutoxyphthalonitrile (**3b**)[19] 2,3-dicyano-5,6-dimethylpyrazine (**5**),[20] 2,3-dicyanonaphthalene (**7**),[21] 1,2-dicyanophenanthrene (**9**).[22]

*4.2.1 General procedure for the synthesis of alkoxy- and phenoxy-substituted phthalonitriles **1c–k***

A mass of 8·65 g (50 mmole) **1b** and an excess of phenolic or alcoholic component (75 mmole phenolic, 100 mmole alcoholic compound) were dissolved in 100 ml dry DMSO under nitrogen; 100 mmole dry potassium carbonate was added, and the mixture was stirred at room temperature. After 4 h and 24 h, the same amount of K_2CO_3 was added. After a total reaction time of 48 h, the mixture was poured into 500 ml dil. HCl, thereby precipitating the product, which was then filtered. The products were purified by dissolving either in ethanol for **1e**, **g**, **i–k** or in acetone for **1d**, **f**, in both cases in the presence of activated charcoal; filtration of the solutions into water caused the white products to precipitate: **1c** was recrystallized from CCl_4 and **1h** from CH_2Cl_2/CCl_4.[11] Replicated reactions gave reproducible yields of over 90% for phenoxy-substituted phthalonitriles and of approximately 60% for alkoxy-substituted species: **1c**: m.p. 103–104°C; MS 220 (M^+, 100%). **1d**: m.p. 120–122°C; MS 276 (M^+, 18%), 261 (100%). **1e**: m.p. 155°C; MS 265 (M^+, 100%). **1f**: m.p. 83–84°C; MS 250 (M^+, 100%). **1g**: m.p. 125–126°C; MS 221 (M^+, 93%), 78 (100%). **1h**: m.p. 165–166°C; MS 236 (M^+, 100%). **1i**: m.p. 144–145°C; MS 158 (M^+, 100%). **1j**: m.p. 134°C; MS 172 (M^+, 22%), 144 (100%). **1k**: m.p. 74–75°C; MS 186 (M^+, 26%), 144 (100%).

*4.2.2 General procedure for the synthesis of phthalocyanines **2** in bulk*

The procedure was as follows: 1 mmole phthalonitrile **1** and the amount of basic coreactant given in Table 1 were placed in an ampoule. The ampoule was degassed by three freeze–thaw cycles and sealed *in vacuo*. The ampoule was heated for a certain time and at a temperature also given in Table 1. In the case of the reactions in the presence of $CuCl_2$, this material was added as an anhydrous salt together with the phthalonitrile in a molar ratio $1 : CuCl_2 = 4 : 1$. After cooling, the ampoules were opened, and the hard, brittle product was ground in a mortar. The products were treated with ethanol in a Soxhlet extractor until the solvent was colorless. This method is valid for metal-free and metal-containing species. The products were dried over P_4O_{10} *in vacuo* at 150°C. Yields are reported in Table 1.

*4.2.3 General procedure for the synthesis of **2**, **4**, **6**, **8**, **10** in solution*

The procedure was as follows: 5 mmole dinitrile and an equimolar amount of basic coreactant were heated in 20 ml dry n-pentanol under reflux. For the reactions in the presence of metal salts, 1·25 mmole were added as an anhydrous salt together with the dinitrile. After 36 h, methanol (50 ml) was added, and the mixture was stirred for 30 min. The isolated reaction products were washed with water and methanol and then treated with methanol in a Soxhlet extractor overnight. The products were dried over P_4O_{10} *in vacuo* at 150°C. Yields are reported in Table 2.

UV–VIS **2a–k** in pyridine (other solvents in brackets), λ (nm), ($\log \varepsilon$):

2a (2H) 694 (5·21), 659 (5·18), 640 (4·62), 602 (4·43). **2b** (2H) 684, 662, 618, 349. **2c** (2H) 703 (4·73), 669 (4·68), 638 (4·30), 609 sh (4·17), 340 (4·55). **2d** (2H) 704 (5·14), 670 (5·11), 640 (4·66), 608 (4·51), 348 (4·84). **2e** (2H) 699 (4·68), 666 (4·64), 640 (2·22), 606 (4·09), 341 (4·54). **2f** (2H) 705 (4·70), 672 (4·66), 640 (4·36), 608 (4·25), 396 sh (443), 344 (4·64). **2g** (2H) 700 (4·90), 666 (4·85), 636 (4·49), 608 (4·33), 346 (4·72). **2h** (2H), 713 (4·77), 684 (4·73), 646 (4·40), 620 sh (4·34), 420 sh (4·42), 345 (4·63). **2i** (2H) 705 (4·73), 671 (4·67), 642 (4·31), 608 (4·17), 390 sh

(4·35), 346 (4·59). **2j** (2H) 707 (4·71), 671 (4·66), 642 (4·32), 609 (4·21), 392 sh (4·36), 346 (4·56). **2k** (2H) 707 (4·72), 672 (4·68), 642 (4·40), 609 sh (4·31), 392 sh (4·49), 346 (4·65). **4a** (2H) 654, 688. **4b** (2H) 346, 424, 603 (sh), 662, 698. **4b** (Cu) 676, 611 (sh), 337 (CH_2Cl_2). **4b** (Co) 670 (CH_2Cl_2). **4b** (Pb) 716, 402, (CH_2Cl_2). **4b** (Zn) 677, 341 (CH_2Cl_2). **4b** (Sn) 676, 611 (sh), 408, 338 (CH_2Cl_2). **6** 648 (5·11), 612 (4·82), 335 (CH_2Cl_2). **8** 780 (1-chloronaphthalene). **10** (2H) 777 (DMF). **10** (Cu) 630 (5·44) (Py).

ACKNOWLEDGEMENT

Part of this work was supported by the Bundesminister für Forschung und Technologie, Federal Republic of Germany, under Grant No. 0328963A.

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