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Cerium-promoted formation of metal-free phthalocyanines

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Abstract—Treatment of phthalonitriles with 6 mol% of $CeCl_3$ or $Ce(acac)_3$ (acac = acetylacetonate) in refluxing 1-pentanol affords the corresponding metal-free phthalocyanines in moderate yields. This non-alkaline pathway is complementary to the base-promoted cyclization methods which are commonly employed in the synthesis of phthalocyanines. Addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) greatly shortens the reaction time and increases the yield of these reactions.

Phthalocyanines represent an important class of functional dyes.[1] Their characteristic blue–green color and robustness allowed their traditional use as industrial pigments. Their usage, however, has been much extended recently to many high technological avenues. With appropriate substitution, phthalocyanines can function as optical recording materials,[2] optical limiters,[3] field-effect transistors,[4] catalysts for photo- or oxidative-degradation of pollutants,[5] and photosensitizers for photodynamic therapy,[6] etc. The synthetic methodologies for this class of compounds are relatively well established. The metal-free analogues, which can serve as the precursors for various metallophthalocyanines, are usually prepared by base-promoted cyclization of phthalonitriles. Some typical procedures involve the treatment with DBU[7] or lithium metal in alcohol (followed by acidic work-up),[8] and reaction in *N*,*N*-dimethylethanolamine under an atmosphere of ammonia.[9] Preparation of metal-free phthalocyanines under non-alkaline conditions is extremely rare.[10] We report herein a new and general approach to this class of macrocyclic compounds using a cerium(III) salt as a promoting agent.

The new methodology involves the treatment of phthalonitriles with 6 mol% of anhydrous $CeCl_3$[11] in 1-pentanol at ca. 160°C for 24–72 h. Under these conditions, a range of phthalonitriles with different functionalities including nitro, alkoxy, thioalkoxy, and amino groups were converted into the corresponding metal-free phthalocyanines in 20–64% yield (Table 1). The yields of these products were comparable, if not better than those obtained by typical base-promoted cyclization reactions.[12] This method, however, could not be applied to 3,6-dialkoxyphthalonitriles or tetrafluorophthalonitrile (**1i**); no significant amount of phthalocyanines could be isolated for these dinitriles. The phthalocyanines **2a**–**h** were purified either by Soxhlet extraction (for **2a** and **2c**) or by column chromatography (for the other phthalocyanines), and characterized using various spectroscopic methods.[13]

As DBU can also promote the tetramerization of phthalonitriles,[7] we examined the effects of this strong base on these cerium-promoted reactions. It was found that the addition of ca. 4 equiv. of DBU can greatly shorten the reaction time (to 6–24 h) and increase the reaction yield (Table 1). Under these conditions, tetrafluorophthalonitrile (**1i**) could also be cyclized to give **2i** in 73% yield. In comparison to the cyclization reactions promoted solely by DBU,[7,14] these reactions generally proceed faster and give higher yields of product, showing that the cerium(III) salt plays an essential role in enhancing the formation of metal-free phthalocyanines. Apart from phthalonitriles, 1,3-diiminoisoindoline derivatives could also be used as the precursors. Thus, treatment of the 1,3-diiminoisoindoline analogue of **1f** with $CeCl_3$ in refluxing 1-pentanol gave **2f** in 45% (24 h, in the absence of DBU) or 53% yield (8 h, in the presence of DBU).

Due to the high solubility of **2b** and the ease of purification of this compound by column chromatography, the conversion of **1b** to **2b** was examined in detail under different reaction conditions (Table 2). It is worth noting that treatment of **1b** with lithium in

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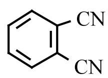
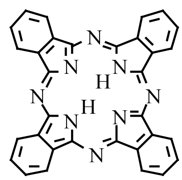
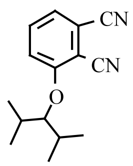
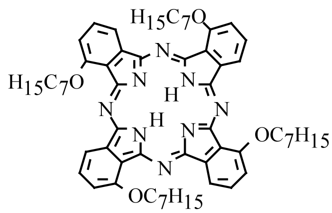
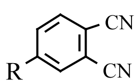
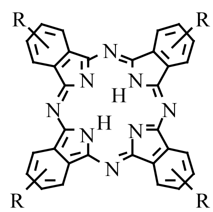
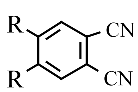
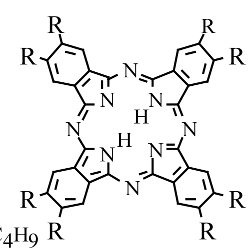
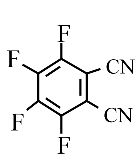
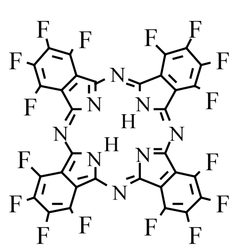
Table 1. Cerium-promoted cyclization of phthalonitriles[a]

		Without DBU		With 4 equiv. of DBU	
Phthalonitrile	Phthalocyanine	Time (h)	Yield (%)	Time (h)	Yield (%)
 **1a**	 **2a**	24	45	—	—
 **1b**	 **2b**	24	52[b]	24	71[b]
 **1c** R = NO_2; **1d** R = $OCH_2CH_2N(CH_3)_2$; **1e** R = $OCH(CH_2CH_3)_2$					
	2c R = NO_2	24	64	—	—
	2d R = $OCH_2CH_2N(CH_3)_2$	48	20	10	70
	2e R = $OCH(CH_2CH_3)_2$	72	38	24	52
 **1f** R = O-*n*-C_5H_{11}; **1g** R = S-*n*-$C_{12}H_{25}$; **1h** R = $S(CH_2CH_2O)_2$-*n*-C_4H_9					
	2f R = O-*n*-C_5H_{11}	24	42	8	53
	2g R = S-*n*-$C_{12}H_{25}$	72	48	6	62
	2h R = $S(CH_2CH_2O)_2$-*n*-C_4H_9	24	42	8	76
 **1i**	 **2i**	48	0	24	73

[a] In the presence of 6 mol% $CeCl_3$ in refluxing 1-pentanol. [b] For a mixture of **2b** and its constitutional isomers.

1-pentanol did not lead to the formation of **2b**. It can be seen in entries 1–4 (Table 2) that the reaction yield is greatly affected by the amount of $CeCl_3$ used. About 6 mol% of $CeCl_3$ with respect to the dinitrile **1b** seems to be the optimum conditions. If the reaction proceeded by a cerium-induced tetramerization followed by removal of the metal center, a higher yield would be expected when a larger amount of $CeCl_3$ (ca. 0.25

Table 2. Conversion of **1b** to **2b** in 1-pentanol

Entry	Cerium salt (mol%)[a]	DBU (equiv.)[a]	Temp. (°C)	Time (h)	Yield (%)[b]
1	$CeCl_3$ (12)	4	160	24	18
2	$CeCl_3$ (6)	4	160	24	71
3	$CeCl_3$ (3)	4	160	24	47
4	$CeCl_3$ (1.5)	4	160	24–48	0
5	$CeCl_3$ (6)	8	150	24	56
6	$CeCl_3$ (6)	8	120	24	37
7	$CeCl_3$ (6)	8	150	48	69
8	$CeCl_3$ (6)	8	120	48	52
9	$Ce(acac)_3$ (12)	4	160	24	9
10	$Ce(acac)_3$ (6)	4	160	24	56
11	$Ce(acac)_3$ (3)	8	160	48	15

[a] With respect to phthalonitrile **1b**.
[b] For a mixture of **2b** and its constitutional isomers.

equiv.) was used, however, the reverse was observed (entries 1–2). The addition of a larger amount of $CeCl_3$ led to the isolation of a substantial amount of the double-decker complex $Ce[Pc(OC_7H_{15})_4]_2$, which was characterized by UV–vis (λ_{max} = 315, 624, and 682 nm in $CHCl_3$) and mass spectrometry. The L-SIMS spectrum showed the M+1 peak at *m*/*z* 2078.9 together with successive losses of C_7H_{15} fragments (*m*/*z* 1979.8, 1880.6, 1781.5). These results suggest that the cerium-(III) salt functions as a catalyst rather than simply a template.

As expected, the yield of **2b** increases with temperature (entries 2, 5 and 6) and the reaction time (entries 5–8). Apart from anhydrous $CeCl_3$, $Ce(acac)_3$[11] can also be used as the catalyst (entries 9–11), but the efficiency in promoting this cyclization is generally lower than that of $CeCl_3$ (compared with entries 1–3). We also attempted the conversion of **1b** to **2b** in 1-chloronaphthalene instead of 1-pentanol. The reactions, in the presence or absence of DBU, did not lead to the expected product, showing that 1-pentanol plays an important function in the catalytic cycle.

In summary, we have developed a convenient method to prepare metal-free phthalocyanines under neutral conditions. This procedure is complementary to the commonly used base-promoted cyclization reactions in the preparation of this important class of functional dyes.

Acknowledgements

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13. Selected data for **2b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.10 (d, $J=7.5$ Hz, 4H, Ar-H), 8.08 (t, $J=7.5$ Hz, 4H, Ar-H), 7.72 (d, $J=7.5$ Hz, 4H, Ar-H), 4.70 (t, $J=5.4$ Hz, 4H, OCH), 2.57–2.68 (m, 8H, CH), 1.52 (d, $J=6.6$ Hz, 24H, Me), 1.22 (d, $J=6.6$ Hz, 24H, Me), −0.06 (br s, 2H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz) δ 158.9, 150.3 (two overlapping signals), 140.2, 130.9, 123.9, 115.1, 114.0, 89.6, 29.7, 20.4, 18.5; L-SIMS m/z 970.6 (M^+); UV–vis ($CHCl_3$) [λ_{max}, nm (log ε)] 319 (4.69), 633 (4.38), 667 (4.51), 700 (5.02), 731 (5.05). Anal. calcd for $C_{60}H_{74}N_8O_4$: C, 74.20; H, 7.68; N, 11.54. Found: C, 73.97; H, 7.70; N, 11.14%. **2e**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.16–9.24 (m, 4H, Ar-H), 8.78–8.79 (m, 4H, Ar-H), 7.69–7.73 (m, 4H, Ar-H), 4.81–4.85 (m, 4H, OCH), 2.04–2.09 (m, 16H, CH_2), 1.23–1.29 (m, 24H, Me), −0.89 (br s, 2H, NH); L-SIMS m/z 858.5 (M^+); UV–vis ($CHCl_3$) [λ_{max}, nm (log ε)] 344 (4.87), 393 (4.58), 611 (4.45), 646 (4.65), 672 (5.06), 709 (5.13). **2h**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.88 (s, 8H, Ar-H), 4.09 (t, $J=6.6$ Hz, 16H, OCH_2), 3.79–3.82 (m, 16H, OCH_2), 3.65–3.70 (m, 32H, OCH_2), 3.44 (t, $J=6.7$ Hz, 16H, SCH_2), 1.51 (quintet, $J=7.1$ Hz, 16H, CH_2), 1.21–1.33 (m, 16H, CH_2), 0.80 (t, $J=7.3$ Hz, 24H, Me), −2.60 (br s, 2H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz) δ 148.3, 140.2, 133.5, 122.1, 71.3, 70.6, 70.1, 69.8, 33.9, 32.7, 19.2, 13.8; L-SIMS m/z 1922.6 (M^+); UV–vis ($CHCl_3$) [λ_{max}, nm (log ε)] 326 (4.57), 361 (4.61), 440 (4.31), 631 (4.29), 666 (4.41), 698 (4.94), 730 (5.01).

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