New approach to the suppression of phthalocyanine aggregation: synthesis of cobalt phthalocyanine complexes containing intramolecular bridges based on 2,7-disubstituted 9,9-bis(2,3-dicyanophenoxymethyl)fluorenes and study of their physical and catalytic properties

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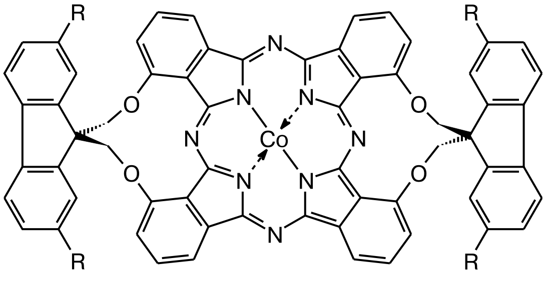
A series of new cobalt monophthalocyanine complexes containing intramolecular bridges between the C(1(11)) and C(25(15)) carbon atoms of phthalocyanine with perpendicular rigid fluorenyl substituents was synthesized from 2,7-di(H,Bu^t)-9,9-bis(2,3-dicyanophenoxymethyl)fluorenes. The spectral and catalytic properties of the synthesized complexes and cobalt 1,8(11),15(18),22(25)-tetraethoxyphthalocyaninate were studied.

Key words: bisphthalodinitriles, phthalonitriles, cobalt phthalocyanines, oxidation, electronic absorption spectra.

In recent time, phthalocyanine complexes became very popular in different areas of science and technology. Due to many useful physical and chemical properties, these complexes found use in optical[1,2] and semiconducting[3] devices, electrochemistry,[4] catalysis,[5] and analytical chemistry.[6,7] The main disadvantage of using phthalocyanines is their enhanced affinity to aggregation and often, as a consequence, low solubility. The main method for the suppression of this phenomenon is the introduction of additional bulky or dendrimeric substituents into the phthalocyanine ring.[8—10]

In this work, we proposed an alternative method for the suppression of aggregation by the creation of a rigid structure with proportional substituents perpendicular (orthogonal) to the phthalocyanine ring, which can strongly prevent aggregation, *i.e.*, formation of an infinite structure formed of parallel phthalocyanine rings. Based on this concept, we obtained the series of phthalocyanines, each containing two substituted or two unsubstituted fluorenyl moieties, and showed that aggregation in these phthalocyanines is completely suppressed.



1, 2

R = H (**1**), Bu^t (**2**)

This model was chosen due to two factors: simplicity of the synthesis and a possibility to realize the proposed concept with the maximum efficiency. In addition, as shown by the theoretical calculation, *tert*-butyl groups substantially elongate the orthogonal substituent (fluorenyl moiety) to make it, in addition, more bulky.

Fluorene and 2,7-di-*tert*-butylfluorene (**3**) [11] were used for the synthesis of the respective 9,9-bishydroxymethylfluorenes **4** [12] and **5** (Scheme 1). The synthesis of **5** consists of the successive metallation of both H(9) protons in **3** with butyllithium followed by formaldehyde addition.

Starting bisphthalodinitriles **7** and **8** for the synthesis of phthalocyanines were obtained by the reactions of 3-nitrophthalodinitrile (**6**) [13] with compounds **4** and **5**. 9,9-Bis(2,3-dicyanophenoxymethyl)fluorene (**7**) was synthesized in the presence of K_2CO_3 [14] in 54% yield. Under these conditions, *tert*-butylated analog **5** reacts incompletely to give only monosubstituted product **8**. The target bisphthalodinitrile **9** was synthesized in a high yield (69%) using NaH as a base (see Scheme 1).

Resulting bisphthalodinitriles **7** and **9** with $Co(OAc)_2 \cdot 4\,H_2O$ were refluxed in an *o*-dichlorobenzene (DCB)—isoamyl alcohol (Am^{i}OH) (4 : 1) mixture in the presence of DBU for 3 h to form cobalt 1,25:11,15-bis(2,7-

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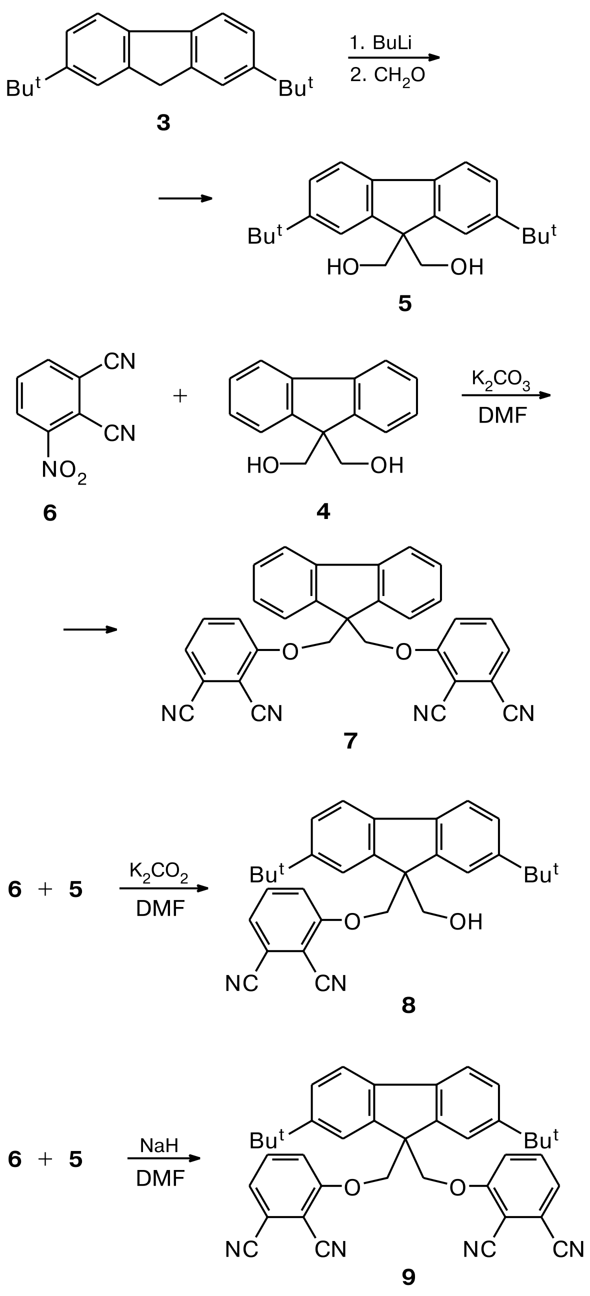
Scheme 1



di(R)fluorene-9,9-diyldimethoxy)phthalocyaninates (R = H (**1**), Bu^t (**2**)). The synthesis of the unsubstituted analog also afforded the product of trimerization of bisphthalodinitrile with one cobalt atom (**10**), and its yield was threefold higher than that of the target complex (Scheme 2).

The tetramerization of 3-ethoxyphthalodinitrile (**11**) gave cobalt 1,8(11),15(18),22(25)-tetraethoxyphthalocyaninate (**12**) (Scheme 3) to be used in subsequent catalytic studies. Compound **11** was obtained from **6** by the method analogous to that described previously.[15] It is assumed[15] that a mixture of several isomers is produced by the tetramerization of compounds of the type of **11**.

Isolated phthalocyanines **1**, **2**, **10**, and **12** are dark blue powders noticeably soluble in organic solvents: 0.005 g mL^{-1} for **1**, 0.035 g mL^{-1} for **2**, 0.008 g mL^{-1} for **10**, and 0.075 g mL^{-1} for **12** (in toluene as the solvent). The presence of *tert*-butyl groups in complex **2** decreases considerably its tendency to aggregation, which is indicated by its higher solubility compared to the solubility of complex **1**.

The structures of all intermediates were proved by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The resulting phthalocyanines were characterized by electronic absorption spectroscopy (EAS), MALDI-TOF mass spectrometry, and elemental analysis. The IR spectrum of derivative **10** contains a signal at 2233 cm^{-1}, indicating the presence of nitrile groups in the structure, and confirms the structure proposed.

The mass spectra of the synthesized phthalocyanines contain intense signals of molecular ions, *m/z*: 1015 (**1**), 1241 (**2**), 1494 (**10**), and 747 (**12**) with the characteristic ratio of isotopomers.

The electronic absorption spectra of phthalocyanines are characterized by the intense Q band at 680—686 nm inherent in Pc^{2-} and corresponding to the electron transition between the π- and π*-orbitals. The spectrum of derivative **10** exhibits the long-wave bathochromic shift of the Q band by 13 nm.

The EAS study of the behavior of complexes **1** and **2** in solutions revealed a linear concentration dependence of the absorbance of the solution in a wide concentration interval (10^{-4}—10^{-6} mol L^{-1}) for both complexes (Fig. 1), indicating the absence of aggregation in solutions of these complexes.

The catalytic properties of the phthalocyanines synthesized were studied. The homogeneous oxidation of styrene by air oxygen in the presence of NaBH$_4$ catalyzed by the synthesized complexes was chosen for the study, using an analogy with the available data.[16]

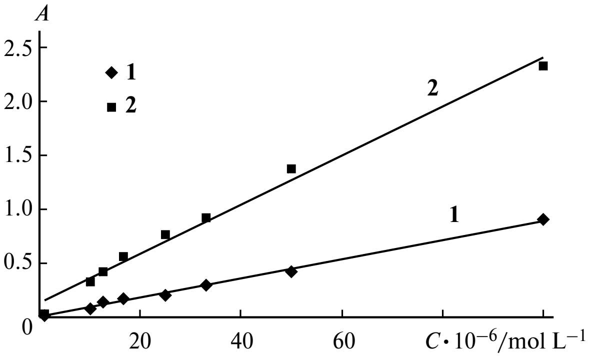
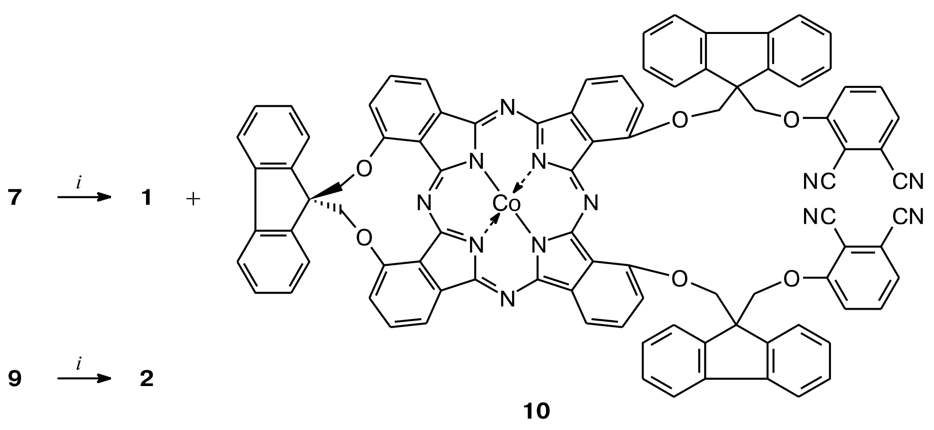


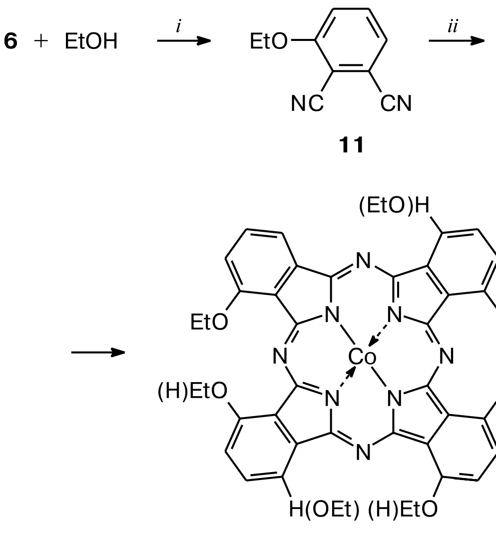
Fig. 1. Plots of the absorbance of solutions of complexes **1** and **2** *vs.* concentration.

Scheme 2

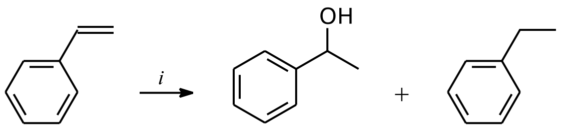


i. DCB : Am^{i}OH = 4 : 1, DBU, Co(OAc)$_2$

Scheme 3



i. K_2CO_3, DMF. *ii*. DCB : Am^{i}OH = 4 : 1, DBU, Co(OAc)$_2$.



i. EtOH, $NaBH_4$, Pc(Co), O_2.

Under these conditions, a by-product, *viz*., ethylbenzene, is formed along with the main reaction product (2-phenylethanol). The mechanism of formation of both products is discussed in detail.[16,17]

To compare the activity and to reveal common regularities, we studied tetraethoxy-substituted cobalt phthalocyanine **12** with the similar electron environment.

The obtained kinetic curves (Fig. 2) demonstrate both the rate and completeness of the reaction. As can be seen,

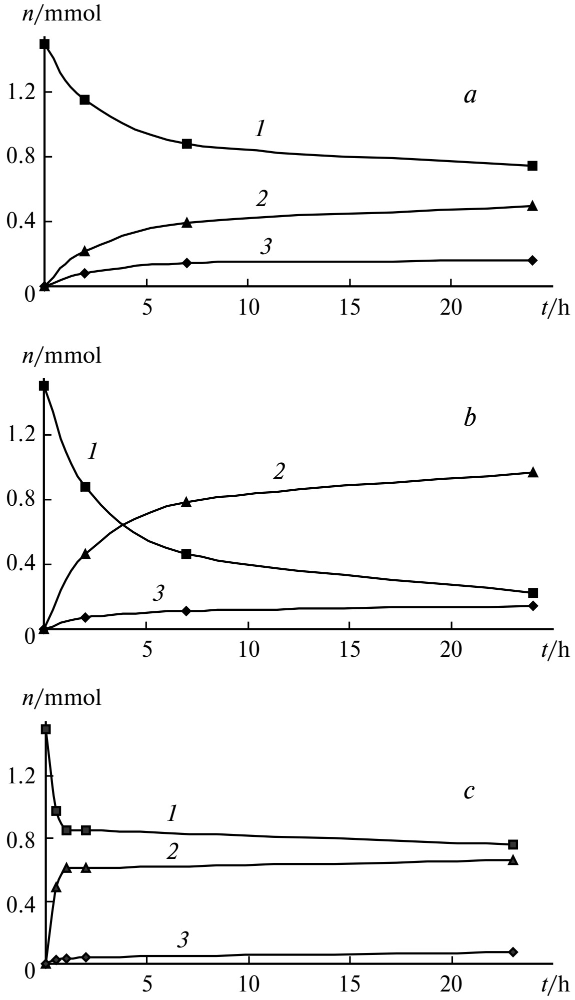


Fig. 2. Kinetic curves obtained using complexes **1** (*a*), **2** (*b*), and **12** (*c*) as catalysts: *1*, styrene; *2*, phenylethanol; and *3*, ethylbenzene.

the activity of the complexes decreases in the series **12** > **2** > **1**, which is indicated by a higher rate of formation of 2-phenylethanol and ethylbenzene at the initial step of the reaction. This dependence can be explained by the open character of the coordination sphere of the metal in the complex. The catalytic activity of all complexes decreases in the reaction course. This is explained, first, by the instability of the phthalocyanine complexes under homogeneous catalytic conditions.[16] The stability of the complexes increases in the series **12** ≪ **1** < **2**. This is clearly seen from the slope of the kinetic curve at the final reaction step (see Fig. 2). This fact demonstrates a higher stability of new complexes **1** and **2** compared to that of tetraethoxy derivative **12**.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 instrument (400 MHz) in $CDCl_3$ or $(CD_3)_2SO$. The chemical shifts are presented in the δ scale relatively to Me_4Si. Thin-layer chromatography was carried out on Silufol UV-254 plates. MALDI-TOF mass spectra (method of matrix-assisted laser desorption and ionization with time-of-flight mass analyzer) were detected on VISION-2000 instruments. Elemental analysis was carried out on a CHN analyzer (Carlo-Erba). Electronic absorption spectra were recorded in the 190—1100 nm region on a Helios-α spectrophotometer.

All solvents were purified and dried prior to use according to standard procedures.[18] A standard 15% solution of BuLi in hexane (Merck) was used for the synthesis of compound **5**. Solid paraform (high-purity grade) was preliminarily dried *in vacuo* at room temperature. A 60% suspension of NaH in paraffinic oil (Merck) was used for the synthesis of compound **9**.

2,7-Di-*tert*-butylfluorene 3 was synthesized by a described procedure.[11]

9,9-Bis(hydroxymethyl)fluorene (4) was synthesized by a known procedure.[12]

2,7-Di-*tert*-butyl-9,9-bis(hydroxymethyl)fluorene (5). A 1.6 *M* solution of BuLi (22.5 mL, 36 mmol) was added dropwise in an argon flow to an ice-cooled solution of compound **1** (10 g, 36 mmol) in anhydrous THF (150 mL). After 5 min, dry paraform (1.11 g, 36 mmol) was introduced into the reaction mixture. Cooling was stopped, and the mixture was stirred for 3 h. Then a 1.6 *M* solution of BuLi (22.5 mL, 36 mmol) was added dropwise with cooling. After 5 min, the second portion of paraform of (1.11 g, 36 mmol) was added. After 12 h, the reaction mixture was poured into a solution of $NaHCO_3$ (120 mL), and the resulting mixture was extracted with Et_2O (3×50 mL). The joint organic fraction was washed with a solution of NaCl and dried over $MgSO_4$. A viscous liquid obtained after solvent evaporation was recrystallized from hexane. The yield was 75%. M.p. 219—221 °C. ^{1}H NMR ($CDCl_3$), δ: 1.39 (s, 18 H, 6 CH_3); 1.98 (s, 2 H, 2 OH); 4.03 (s, 4 H, 2 CH_2); 7.46 (d, 2 H, H(3), H(6), J = 8.1 Hz); 7.62 (s, 2 H, H(1), H(8)); 7.67 (d, 2 H, H(4), H(5), J = 8.1 Hz). ^{13}C NMR, δ: 31.52 ($C(\underline{Me})_3$); 34.84 ($\underline{C}(Me)_3$); 57.45 ($(C(9)_{flu})$); 66.91 (CH_2); 119.37, 120.93, 125.15 (3 CH); 138.33, 145.64, 150.13 (6 C_{flu} quatern.). Calculated (%): C, 81.67; H, 8.87. $C_{23}H_{30}O_2$. Found (%): C, 81.37; H, 8.86.

3-Nitrophthalodinitrile (6) was synthesized by a known procedure.[13]

9,9-Bis(2,3-dicyanophenoxymethyl)fluorene (7). A mixture of compound **4** (2 g, 8.85 mmol), compound **6** (3.5 g, 20.23 mmol), anhydrous DMF (20 mL), and anhydrous K_2CO_3 (6.0 g, 43.47 mmol) was stirred for 120 h in an argon atmosphere at ~20 °C. Then the mixture was poured into water. The precipitate formed was filtered off, washed with water, and dried at 70 °C. The resulting product was purified by column chromatography on silica gel (toluene—AcOEt (8 : 1) mixture as the eluant, R_f 0.69). The yield was 54%. M.p. 265 °C. ^{1}H NMR ($CDCl_3$), δ: 4.55 (s, 4 H, 2 CH_2); 7.32, 7.40 (both d, 2 H each, 2 CH, J = 8.2 Hz); 7.46, 7.54 (both t, 2 H each, 2 CH_{flu}, J = 7.5 Hz); 7.69 (t, 2 H, 2 CH, J = 8.2 Hz); 7.86, 8.11 (both d, 2 H each, 2 CH_{flu}, J = 7.5 Hz). ^{13}C NMR, δ: 53.25 ($C_{flu}(9)$); 70.36 (CH_2); 104.61, 113.32 (2 $\underline{C}$—CN); 114.99, 116.66 (2 CN); 116.88, 120.34, 125.61, 127.94 (4 CH_{flu}); 126.00, 129.25, 134.95 (3 CH); 140.60, 142.96 (4 C_{flu} quatern.); 160.79 ($\underline{C}$—O). Calculated (%): C, 77.83; H, 3.76; N, 11.71. $C_{31}H_{18}N_4O_2$. Found (%): C, 77.79; H, 3.91; N, 11.40.

The formation of product **8** was monitored by NMR. The spectrum of the reaction mixture contained two characteristic singlets of nonequivalent methylene protons: δ_H 4.19 and 4.38 ($CDCl_3$).

2,7-Di-*tert*-butyl-9,9-bis(2,3-dicyanophenoxymethyl)fluorene (9). A saturated solution of compound **5** (2 g, 5.9 mmol) in DMF was added dropwise to a suspension of NaH (0.6 g, 25 mmol) and anhydrous DMF (30 mL) with vigorous stirring and cooling to −78 °C. After 10 min, a solution of compound **6** (2.15 g, 12.4 mmol) was added dropwise to the reaction mixture under the same conditions. After 0.5 h, cooling was stopped. The reaction mixture was stirred for 12 h and then poured into water. The precipitate formed was filtered off, washed with water, and dried on a filter and then at 70 °C to a constant weight. Then the product was purified by chromatography using a toluene—AcOEt (8 : 1) mixture as the eluant (R_f 0.63). The yield 69%. M.p. 317 °C. ^{1}H NMR ($CDCl_3$), δ: 1.43 (s, 18 H, 6 CH_3); 4.56 (s, 4 H, 2 CH_2); 7.34, 7.39 (both d, 2 H each, 2 CH, J = 7.9 Hz); 7.55 (d, 2 H, 2 CH_{flu}, J = 8.1 Hz); 7.68 (t, 2 H, 2 CH, J = 7.9 Hz); 7.73 (d, 2 H, 2 CH_{flu}, J = 8.1 Hz); 8.08 (s, 2 H, 2 CH_{flu}). ^{13}C NMR, δ: 31.51 ($C(\underline{Me})_3$); 35.12 ($\underline{C}(Me)_3$); 53.33 ($C_{flu}(9)$); 70.68 (CH_2); 104.41, 113.23 (2 $\underline{C}$—CN); 115.04, 116.62 (2 CN); 116.88, 119.54, 125.48 (3 CH_{flu}); 122.76, 126.29, 134.95 (3 CH); 137.97, 143.12 (4 C_{flu} quatern.); 151.21 ($\underline{C}$—$C(Me)_3$); 160.85 ($\underline{C}$—O). Calculated (%): C, 79.33; H, 5.76; N, 9.49. $C_{39}H_{34}N_4O_2$. Found (%): C, 79.31; H, 5.89; N, 9.32.

3-Ethoxyphthalodinitrile (11). A mixture of anhydrous EtOH (0.33 mL, 6.50 mmol), compound **4** (1.0 g, 5.78 mmol), DMF (10 mL), and anhydrous K_2CO_3 (2.0 g, 14.49 mmol) was stirred for 120 h in an argon atmosphere at ~20 °C. Then the reaction mixture was poured into water. The precipitate formed was filtered off and dried at 70 °C. The yield was 78%. M.p. 134 °C. ^{1}H NMR ($CDCl_3$), δ: 1.53 (t, 3 H, CH_3, J = 7.8 Hz); 4.23 (q, 2 H, CH_2, J = 7.8 Hz); 7.24 (d, 1 H, H(6), J = 8.1 Hz); 7.35 (d, 1 H, H(4), J = 8.1 Hz); 7.65 (t, 1 H, H(5), J = 8.1 Hz). ^{13}C NMR, δ: 14.27 (CH_3); 65.52 (CH_2); 104.85, 112.95 (2 $\underline{C}$—CN); 115.26, 116.98 (2 CN); 116.51, 124.81, 134.37 (C(4), C(5), C(6)); 161.21 ($\underline{C}$—NO_2). Calculated (%): C, 69.76; H, 4.65; N, 16.28. $C_{10}H_8N_2O$. Found (%): C, 70.11; H, 4.83; N, 16.13.

Synthesis of cobalt phthalocyaninates 1, 2, and 12 (general procedure). A mixture of dinitriles **7** and **9** (2.10 mmol) or dinitrile **11** (4.20 mmol), $Co(OAc)_2 \cdot 4\ H_2O$ (0.26 g, 1.05 mmol), and DBU (1 mL) was refluxed in a mixture of DCB (40 mL) and isoamyl alcohol (10 mL) to the end of the reaction (2.5—3 h). The reaction course was monitored by TLC. Then the dark blue reaction mixture was concentrated by distilling off the solvent and chromatographed on neutral Al_2O_3 using a toluene—Py (15 : 1) mixture as the eluant. The primary blue fraction was collected. The eluate was concentrated to a volume of 2 mL, and hexane was added. The dark blue precipitate formed was filtered off, washed with hexane, and dried *in vacuo*.

Cobalt 1,25:11,15-bis(fluorene-9,9-diyldimethoxy)phthalocyaninate (1). R_f 0.44 (toluene—Py, (15 : 1) as the eluant). The yield 3%. UV (toluene), λ_{max}/nm (ε): 680 (17700). MS, *m/z*: 1015.0 $[M]^+$. Found (%): C, 73.51; H, 3.78; N, 10.87. $C_{62}H_{36}CoN_8O_4$. Calculated (%): C, 73.30; H, 3.57; N, 11.03.

Cobalt 1,25:11,15-bis(2,7-di-*tert*-butylfluorene-9,9-diyldimethoxy)phthalocyaninate (2). R_f 0.54 (toluene—Py (15 : 1) as the eluant). The yield was 14%. UV (toluene), λ_{max}/nm (ε): 686 (45600). MS, *m/z*: 1241 $[M]^+$. Found (%): C, 75.75; H, 5.98; N, 8.91. $C_{78}H_{68}CoN_8O_4$. Calculated (%): C, 75.48; H, 5.48; N, 9.03.

Complex 10 was obtained along with the chromatographic isolation of compound **1** (R_f 0.65) using a toluene —Py mixture (15 : 1) as the eluant. The yield was 9%. UV (toluene), λ_{max}/nm: 693. MS, *m/z*: 1493 $[M]^+$.

Cobalt 1,8(11),15(18),22(25)-tetraethoxyphthalocyaninate (12). R_f 0.37 (toluene—Py (15 : 1) as the eluant). The yield was 34%. UV (toluene), λ_{max}/nm: 686. MS, *m/z*: 747 $[M]^+$. Found (%): C, 64.75; H, 4.56; N, 14.81. $C_{40}H_{32}CoN_8O_4$. Calculated (%): C, 64.17; H, 4.28; N, 14.97.

Procedure of catalytic experiments. A mixture of anhydrous EtOH (4 mL), $NaBH_4$ (0.10 g, 3 mmol), styrene (0.173 mL, 1.5 mmol), and a solution of the complex (0.015 mmol) in anhydrous THF (0.2 mL) was vigorously stirred in an oxygen atmosphere with periodical sampling for analysis. A taken sample (150 μL) was diluted with pentane (special-purity grade, 2.5 mL). The resulting turbid solution was filtered through a cotton wool layer, which then was washed with pentane (1 mL). A standard solution (1 mL) of 2-fluoroaniline in pentane (2.3 mg mL^{-1}) and Et_3N (0.5 mL) were added to the combined solution. The resulting mixture (5 mL) was shaken, and a sample of 0.2 μL was analyzed by gas chromatography on a Kristall 2000 M chromatograph equipped with a ZB-1 capillary column (15 m×0.53 mm×0.5 μm) with a polydimethylsiloxane coating and a flame-ionization detector. The quantitative calculation was performed using known concentrations of the internal standard 2-fluoroaniline (0.46 mg mL^{-1}).

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