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Synthesis and Characterization of *cis*-A₂B-Type *meso*-Triaryl-Substituted Corroles

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A practical synthesis of cis-A₂B-type 5,10,15-triarylcorroles has been developed that involves [2+2]-type acid-catalyzed condensation of 5-aryldipyrromethane and 5-(pentafluorophenyl)dipyrromethane-1-carbinol and subsequent 2,3-

Introduction

Corroles are 18π aromatic tetrapyrrolic macrocycles, onecarbon missing cousins of porphyrins, bearing a direct pyrrole-pyrrole linkage and three pyrrolic NH protons.^[1] Corroles have been shown to be promising as oxidation catalysts, water oxidation catalysts, and as sensors.^[2] These developments have been encouraged by the seminal synthesis of 5,10,15-tris(pentafluorophenyl)-substituted corrole by Gross et al. in 1999.^[3] Just around the same time, several rational syntheses of corroles have been explored by Gryko and Paolesse, which have contributed significantly to advances in corrole chemistry.^[4,5] Among these, A₃ corroles and *trans*-A₂B corroles have been most extensively prepared through reactions of 5-aryldipyrromethane with aldehydes.^[4,5] Synthesis of ABC-type corroles was also accomplished by oxidation of bilanes (tetrapyrranes) bearing three different meso-aryl substituents.^[6] Despite these efforts, cis-A2B-type corroles have been left almost unexplored.^[7,8] In this paper, we report an effective synthesis of cis-A₂B-type corroles through [2+2] condensation of 5aryldipyrromethanes and a 5-pentafluorophenyldipyrromethane monocarbinol and subsequent oxidative cyclization. This method is reproducible and synthetically important because of the ready availability of 5-aryldipyrromethanes and 5-(pentafluorophenyl)dipyrromethane-1carbinol in large quantities.

Results and Discussion

5-(Pentafluorophenyl)dipyrromethane $(1)^{[9]}$ and its monocarbinol $2^{[10]}$ are useful building blocks in the present

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dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) induced oxidative cyclization. All the corroles thus synthesized were structurally well-characterized, and their optical and electrochemical properties were also studied.

[2+2] strategy for the synthesis of corroles, and they can be prepared in multigram quantities. We first attempted the synthesis of 5,10,15-tris(pentafluorophenyl)corrole (4) by one-pot condensation reaction of 1 with 2 (Scheme 1). The condensation was performed with the aid of acid for 10 min to produce bilane 3, which was directly oxidized with 2,3dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for 1 h. Corrole 4 was isolated by separation through a silica gel column. The nature of the acid was important in this corrole synthesis. The reactions with *p*-toluenesulfonic acid, methanesulfonic acid, or $Dy(OTf)_3$ did not provide 4, whereas BF₃·OEt₂ and trifluoroacetic acid (TFA) were found to produce 4 in 3.8 and 2.3% yields, respectively. However, we could not improve the yields of 4 by one-pot reactions. We then examined the condensation and oxidative cyclization steps separately. The condensation of 1 and 2 with BF_3 ·OEt₂ for 15 min gave bilane 3 in poor yields. However, we found that slow addition of a solution of 2 in CH₂Cl₂ to a mixture of 1 and BF₃·OEt₂ in CH₂Cl₂ over 3 min and subsequent stirring for 5 min, afforded 3 in 59% yield. Whereas the oxidative cyclization of 3 with pchloranil gave 4 in low yield (ca. 6%), the oxidation of 3 with 3 equiv. DDQ in CH₂Cl₂ afforded 4 in 44% yield. Notably, the one-pot reaction sequence combining the optimal conditions of the two steps gave only poor yield of 4. Therefore, based on these results, we set a practical synthetic method as following; (i) a solution of **2** in CH_2Cl_2 was added slowly to a solution of a dipyrromethane and BF₃·OEt₂ in CH₂Cl₂, and the resulting mixture was stirred for 5 min at room temperature; (ii) the intermediate bilane was quickly purified by column chromatography [for 3, $R_{\rm f}$ ≈ 0.3 (hexane/Et₂O, 6:4)]; (iii) semipurified bilane was then oxidized with DDQ for 1 h; (iv) the resulting solution was passed through a short silica gel pad and then purified by silica gel column chromatography. This method is reasonably reproducible, allowing the synthesis of a range of cis- A_2B -corroles, mostly in yields of around 10%.

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Scheme 1. Synthesis of 5,10,15-tris(pentafluorophenyl)corrole by [2+2] condensation of dipyrromethane and dipyromethane mono-carbinol.

By following this synthetic protocol, we synthesized *cis*-A₂B-type corroles bearing various aryl substituents at the 5-position (Scheme 2). Corroles **5** and **6**, bearing sterically hindered 2,6-dichlorophenyl and mesityl substituents, were obtained in 9.6 and 12% yields, respectively. Corrole **7**, with an electron-withdrawing *p*-nitrophenyl substituent, was afforded in 10% yield. 2,4,6-Trimethoxy and 1-naphthyl-substituted corroles **8** and **9** were prepared in 11 and 9.3% yields, respectively. (4,6-Dichloropyrimidin-5-yl)-substituted corrole **10** was obtained in 5.7% yield. It is noteworthy that we only needed the corresponding 5-aryldipyrromethanes for the screening. This is an advantageous aspect as compared with the reported ABC-type corrole synthesis,^[6a] because the latter inevitably required preparation of the corresponding 5,10,15-triaryl-substituted bilanes

through multistep synthesis, with challenging purification required in each step.



Scheme 2. Synthesis of cis-A2B-type corroles.

Fortunately, we have succeeded in determining the X-ray crystal structures of all the cis-A₂B-corroles prepared in this study. The crystal structures are shown in Figure 1 and the structural information is summarized in Table 1. Judging from the C–N–C angles of imine-type (ca. 106°) and amine-type (ca. 110°) pyrroles, we assigned all the three N–H atoms, two of which locates at the bipyrrole-like segments, in agreement with the standard feature of free-base corroles.^[3b,11] The mean plane deviation (MPD) values, defined by the average distance between core 23 atoms and its mean plane, are calculated to be 0.119 Å for **5**, 0.129 Å for **6**,



Figure 1. X-ray crystal structures of (a) 5, (b) 6, (c) 7, (d) 8, (e) 9, and (f) 10. Thermal ellipsoids were scaled to 30% probability level. Solvent molecules were omitted for clarity. One of two independent molecules in the asymmetric unit is shown for 10.

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0.130 Å for 7, 0.144 Å for 8, 0.141 Å for 9, and 0.125 (0.127) Å for 10. These relatively large MPD values are likely derived from steric hindrance of the inner three hydrogen atoms. The dihedral angles (ϕ) of the sterically hindered substituents in 5, 6, 8, 9, and 10 are found in the range of 57–74°, whereas the 4-nitrophenyl substituent in 7 is tilted toward the corrole mean plane by only 39°. Interestingly, intermolecular hydrogen-bonding interactions are observed in the packing structures between the inner N–H protons and the carbonyl oxygen atoms of included acetone in 5, and the inner N–H protons and the nitrogen atoms in the pyrimidine moieties of another molecule in the asymmetric unit in 10 (see Figure 1, see part f and the Supporting Information).

Table 1. Structural details of corroles.

Corrole	5	6	7	8	9	10
φ [°] ^[a]	71.58	69.16	38.61	71.32	57.15	89.68, 81.32
MPD [Å]	0.119	0.129	0.130	0.144	0.141	0.125, 0.127

[a] Dihedral angles of the aryl substituents at the 5-position with regard to the mean plane of corroles.

Corroles exhibit similar but slightly different absorption and emission spectra compared with those of porphyrins. For instance, the parent corrole 4 exhibits Soret-like absorption bands at 407 and 420 nm and Q-like bands in the range of 500-700 nm, and fluorescence in the range of 600-800 nm.^[12] The split Soret-like band and relatively intensified Q-like bands are ascribed to its decreased symmetry. These features are also observed in the absorption spectra of cis-A₂B-type corroles 5–10, except for 7, which shows a distinctly broader Soret-like band at 424 nm and a much broader Q-like band at 581 nm (Figure 2). These broad absorption bands may be ascribed to the intramolecular charge-transfer interaction from the corrole core to the nitrobenzene moiety in 7.^[4b,12] The fluorescence spectra of these corroles are roughly similar, being observed in the range of 643-652 nm, except for the broad and redshifted emission at 671 nm in 7. The fluorescence quantum yields were determined by using a sphere detection instrument and are shown in Table 2. Corroles bearing electron-donating substituents show relatively high fluorescence quantum yields (6, 8, and 9), and those bearing electron-accepting substituents display relatively low fluorescence quantum yields (7 and 10).^[13]

The electrochemical properties were studied by cyclic voltammetry. According to the seminal paper by Kadish et al., tris(pentafluorophenyl)corrole (4) displayed irreversible first oxidation and reduction waves at 0.86 and -1.04 V in benzonitrile against SCE, respectively.^[14] We confirmed the presence of these waves with our instrument using tetrabutylammonium hexafluorophosphate as an electrolyte in benzonitrile at 0.42 and -1.51 V against ferrocene/ferrocenium couple, respectively. After the first oxidation (ox. I, Figure 3), the radical cation of 4 readily transfers a proton to neutral 4, thus generating (Cor)-H₂ and [(Cor)-H₄]⁺, which are oxidized at higher potential (0.52 and 0.75 V, ox. III and IV), respectively (Figure 3). On the other hand, the first



Figure 2. UV/Vis absorption (top) and fluorescence (bottom) spectra of 4-10 in CH₂Cl₂.

Table 2. Optical properties of corroles in CH₂Cl₂.

Corrole	λ_{abs} [nm](log	$g \varepsilon [M^{-1} cm^{-1}])$	$\lambda_{\rm em} \ [nm]^{[a]}$	$\Phi_{\rm F}^{\rm [b]}$
4 5	407 (5.08) 407 (5.14)	561 (4.28), 604 (4.01) 562 (4.34), 602 (4.04)	643 643	0.060 0.059
6	407 (5.08)	563 (4.28), 599 (3.95)	644	0.099
7	424 (5.00)	581 (4.40)	671	0.040
8	410 (5.07)	565 (4.30), 601 (4.08)	652	0.092
9	410 (5.17)	565 (4.38), 600 (4.08)	650	0.094
10	409 (5.14)	564 (4.38), 605 (4.11)	647	0.041

[a] Excited at Soret-like band maxima. [b] Absolute fluorescence quantum yield upon excitation at Soret-band maxima.

reduction of 4 generates $[(Cor)^{-}H_3]^{-}$, from which generation of a hydrogen radical takes place with concurrent formation of $[(Cor)-H_2]^-$ (red. I), which is further reduced at -2.12 V (red. II) and in turn oxidized at -0.16 V (red. III). In our setup, the second reduction wave of 4, which was observed as a weak peak in Kadish's paper, was not detected. Based on these interpretations, the oxidation and reduction potentials of 5–10 have been assigned (Table 3). The first oxidation potentials are positively shifted by 0.20 V in 6 and 0.29 V in 8, due to the electron-donating substituents. In contrast, negatively shifted reduction potentials are observed in 7, that is, the first reduction at -1.30 V, reflecting the strongly electron-accepting property of the 4-nitrophenyl substituent. The second reduction at -1.64 V may be ascribed to reduction of the nitrophenyl moiety.^[15] The electrochemical HOMO-LUMO gaps are calculated as shown in Table 3, which are roughly consistent with the optical HOMO-LUMO gaps estimated by the absorption spectra.

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Figure 3. Cyclic voltammograms of 5 measured in benzonitrile using tetrabutylammonium hexafluorophosphate as an electrolyte.

Table 3. Electrochemical potentials of corroles 4–10 in benzonitrile with 0.1 M Bu₄NPF₆.^[a]

	Oxidation				Reduction			
Corrole	I	II	III	IV	I	Π	III ^[b]	$E [\mathrm{eV}]^{[\mathrm{e}]}$
4	0.42	-0.18	0.52	0.75	-1.51	-2.12 ^[c]	-0.16 ^[c]	1.93
5	0.34	-0.25	0.58 ^[c]	0.72 ^[c]	-1.59	-2.38	-0.24 ^[c]	1.93
6	0.22	-0.22	0.45 ^[c]	0.60 ^[c]	-1.59	-2.32	-0.26 ^[c]	1.81
7	0.29	-0.24	0.52 ^[c]	0.73 ^[c]	-1.30, -1.64,	[c] -2.00[c]	-0.22 ^[c]	1.59
8	0.13		0.32 ^[c]		-1.53 ^[d]	$-2.34^{[d]}$	-0.36 ^[c]	1.66
9	0.22		0.43 ^[c]	0.65 ^[c]	-1.64	-2.29	-0.27 ^[c]	1.86
10	0.34	-0.02	0.55	0.74 ^[c]	-1.50	-2.24	$-0.18^{[c]}$	1.84

[a] Potentials [V] were determined vs. ferrocene/ferrocenium ion by cyclic voltammetry. Working electrode: glassy carbon. Counter electrode: Pt wire. Reference electrode: Ag/AgClO₄. Scan rate: 0.05 V/s. [b] Only detected after the first reduction. [c] Reversible peaks. [d] Determined by differential pulse voltammetry (DPV). [e] Electrochemical HOMO–LUMO gaps.

Conclusions

We have developed a practical and useful synthesis of cis-A₂B-type corroles based on a stepwise protocol consisting of [2+2] acid-catalyzed condensation reaction of 5-aryldipyromethanes with 5-pentafluorophenyldipyrromethane monocarbinol **2** and subsequent oxidative cyclization with DDQ. This method allowed the synthesis of various cis-A₂B-corroles that were difficult to prepare by previous methods. Use of this method for the synthesis of more complex corroles and further synthetic application of cis-A₂Bcorroles to more elaborated functional systems are in progress in our laboratory.

Experimental Section

General Information: Commercially available solvents and reagents were used without further purification, unless otherwise noted. Anhydrous dichloromethane was distilled from CaH₂. Spectroscopic grade solvents were used for all the spectroscopic studies. Silica gel column chromatography was performed on Wakogel C-300. Alumina column chromatography was performed on Sumitomo γ -Alumina KCG-1525W (Blockmann grade II). Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F254 (Merck 5554). UV/Vis absorption spectra were recorded with a Shimadzu UV-3600 spectrometer. Fluorescence spectra were recorded with a Shimadzu RF-5300PC spectrometer. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920-02S. ¹H and ¹⁹F NMR spectra were recorded with a JEOL ECA-600 spectrometer (operating as 600.17 MHz for ¹H and 564.73 MHz for ¹⁹F) using the residual solvent as the internal reference for ¹H (δ = 7.26 ppm in CDCl₃) and hexafluorobenzene as an external reference for ¹⁹F (δ = 162.9 ppm). High-resolution atmospheric-pressure-chemical-ionization time-of-flight mass-spectroscopy (HR-APCI-TOF-MS) was performed with a Bruker micrOTOF model using positive and negative mode. Mass spectra were recorded with a Shimadzu AXIMA-CFRplus using positive-MALDI-TOF method with matrix. Single-crystal X-ray diffraction analysis data were collected at -180 °C with a Rigaku XtaLAB P200 by using graphite-monochromated Cu- K_{α} radiation (λ = 1.54187 Å). The structures were solved by direct methods (SHELXS-97) and refined with full-matrix least-squares technique (SHELXL-97). Redox potentials were measured with an ALS electrochemical analyzer model 660.

General Procedure for the Synthesis of *cis*-A₂B-Corroles: To a solution of dipyrromethane in anhydrous dichloromethane, was added BF_3 ·OEt₂ (0.2 equiv.) in acetonitrile. To this solution was added

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slowly a solution of **2** (1.0 equiv.) in anhydrous dichloromethane over 3 min. The resulting solution was further stirred for 5 min at room temperature. The reaction was quenched with triethylamine and the solvents were evaporated. The crude mixture was quickly purified by silica-gel column chromatography. Note: In the case of **3**, a fraction of $R_{\rm f} = 0.3$ (*n*-hexane/Et₂O, 6:4 v/v) was collected; when a TLC plate was exposed to Br₂, a dipyrromethane band turned to pink and a bilane band turned to brown. The semipurified bilane was dissolved in dichloromethane (ca. 0.7 mM), to which a solution of DDQ (0.8 equiv.) in THF was slowly added and the resulting mixture was stirred for 1 h at room temperature. The reaction mixture was then passed through a short silica-gel pad and the solvent was evaporated. The crude mixture was purified by silica-gel column chromatography (*n*-hexane/dichloromethane and/ or *n*-hexane/toluene) to provide *cis*-A₂B-corroles.

Supporting Information (see footnote on the first page of this article): Experimental details and compound data; NMR spectra; mass spectra; X-ray crystal structures; and cyclic voltammograms.

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- a) R. Paolesse, in: *The Porphyrin Handbook*, vol. 2 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, p. 201–232; b) F.-P. Montforts, M. Glasenapp-Breiling, D. Kusch, in: *Houben-Weyl Methods of Organic Chemistry*, vol. E9d (Ed.: E. Schaumann), Thieme, Stuttgart, New York, **1998**, p. 665–672; c) R. Guilard, J.-M. Barbe, C. Stern, K. M. Kadish, in: *The Porphyrin Handbook*, vol. 18 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Elsevier Science USA, **2003**, p. 303–351.
- a) Z. Gross, H. B. Gray, Adv. Synth. Catal. 2004, 346, 165; b) [2] I. Aviv, Z. Gross, Chem. Commun. 2007, 1987; c) Z. Gross, L. Simkhovich, N. Galili, Chem. Commun. 1999, 599; d) Z. Gross, G. Golubkov, L. Simkhovich, Angew. Chem. Int. Ed. 2000, 39, 4045; Angew. Chem. 2000, 112, 4211;; e) G. Golubkov, J. Bendix, H. B. Gray, A. Mahammed, I. Goldberg, A. J. DiBilio, Z. Gross, Angew. Chem. Int. Ed. 2001, 40, 2132; Angew. Chem. 2001, 113, 2190;; f) L. Simkhovich, A. Mahammed, I. Goldberg, Z. Gross, Chem. Eur. J. 2001, 7, 1041; g) A. Mahammed, Z. Gross, Angew. Chem. Int. Ed. 2006, 45, 6544; Angew. Chem. 2006, 118, 6694; h) A. Haber, A. Mahammed, B. Fuhrman, N. Volkova, R. Coleman, T. Hayek, M. Aviram, Z. Gross, Angew. Chem. Int. Ed. 2008, 47, 7896; Angew. Chem. 2008, 120, 8014; i) I. Aviv, Z. Gross, Chem. Eur. J. 2008, 14, 3995;j) D. J. Graham, D. K. Dogutan, M. Schwalbe, D. G. Nocera, Chem. Commun. 2012, 48, 4175; k) D. K. Dogutan, R. McGuire, D. G. Nocera, J. Am. Chem. Soc. 2011, 133, 9178
- [3] a) Z. Gross, N. Galili, I. Saltsman, Angew. Chem. Int. Ed. 1999, 38, 1427; Angew. Chem. 1999, 111, 1530; b) Z. Gross, N. Galili, L. Simkhovich, I. Saltsman, M. Botoshansky, D. Bläser, R. Boese, I. Goldberg, Org. Lett. 1999, 1, 599; c) R. Paolesse, L. Jaquinod, D. J. Nurco, S. Mini, F. Sagone, T. Boschia, K. M. Smith, Chem. Commun. 1999, 1307.
- [4] a) R. Paolesse, S. Nardis, F. Sagone, R. G. Khoury, J. Org. Chem. 2001, 66, 550; b) R. Paolesse, A. Marini, S. Nardis, A. Froiio, F. Mandoj, D. J. Nurco, L. Prodi, M. Montalti, K. M.

Smith, J. Porphyrins Phthalocyanines 2003, 7, 25; c) D. T. Gryko, J. P. Fox, D. P. Goldberg, J. Porphyrins Phthalocyanines 2004, 8, 1091; d) R. Paolesse, Synlett 2008, 2215; e) C. M. Lemon, P. J. Brothers, J. Porphyrins Phthalocyanines 2011, 15, 809.

- [5] a) D. T. Gryko, K. Jadach, J. Org. Chem. 2001, 66, 4267; b) C. V. Asokan, S. Smeets, W. Dehaen, Tetrahedron Lett. 2001, 42, 4483; c) D. T. Gryko, K. E. Piechota, J. Porphyrins Phthalocyanines 2002, 6, 81; d) B. Andrioletti, E. Rose, J. Chem. Soc. Perkin Trans. 1 2002, 715; e) D. T. Gryko, B. Koszarna, Org. Biomol. Chem. 2003, 1, 350; f) D. T. Gryko, B. Koszarna, Synthesis 2004, 2205; g) R. Goldschmidt, I. Goldberg, Y. Balazs, Z. Gross, J. Porphyrins Phthalocyanines 2006, 10, 76; h) M. Tasior, D. T. Gryko, Heterocycles 2007, 71, 2735; i) B. Koszarna, R. Voloshchuk, D. T. Gryko, Synthesis 2007, 1339; j) D. T. Gryko, J. Porphyrins Phthalocyanines 2008, 12, 906; k) M. Tasior, D. T. Gryko, M. Cembor, J. S. Jaworski, B. Venturac, L. Flamigni, New J. Chem. 2007, 31, 247; 1) I. Saltsman, M. Botoshansky, Z. Gross, Tetrahedron Lett. 2008, 49, 4163; m) H.-Y. Zhan, H.-Y. Liu, H.-J. Chen, H.-F. Jiang, Tetrahedron Lett. 2009, 50, 2196; n) M. Tasior, D. T. Gryko, D. J. Pielacińska, A. Zanelli, L. Flamigni, Chem. Asian J. 2010, 5, 130; o) T. H. Ngo, F. Nastasi, F. Puntoriero, S. Campagna, W. Dehaen, W. Maes, J. Org. Chem. 2010, 75, 2127.
- [6] a) R. Guilard, D. T. Gryko, G. Canard, J.-M. Barbe, B. Koszarna, S. Brandès, M. Tasior, *Org. Lett.* **2002**, *4*, 4491; b) G. R. Geier III, J. F. B. Chick, J. B. Callinan, C. G. Reid, W. P. Auguscinski, *J. Org. Chem.* **2004**, *69*, 4159; c) O. A. Egorova, O. G. Tsay, S. Khatua, J. O. Huh, D. G. Churchill, *Inorg. Chem.* **2009**, *48*, 4634.
- [7] [2+2]-Type synthesis of core-modified corroles has been reported by Lee et al., however, attempts to prepare *cis*-A₂B corroles were unsuccessful, see: a) W.-S. Cho, C.-H. Lee, *Tetrahedron Lett.* 2000, 41, 697; b) C.-H. Lee, W.-S. Cho, J.-W. Ka, H.-J. Kim, P. H. Lee, *Bull. Korean Chem. Soc.* 2000, 21, 429; c) D. T. Gryko, *Eur. J. Org. Chem.* 2002, 1735.
- [8] [2+2]-Type condensation of dipyrromethane and bipyrrole has been reported, see: a) R. A. Decréau, J. P. Collman, *Tetrahedron Lett.* 2003, 44, 3323; b) G. R. Geier III, S. C. Grindrod, *J. Org. Chem.* 2004, 69, 6404; c) K. C. Braaten, D. G. Gordon, M. M. Aphibal, G. R. Geier III, *Tetrahedron* 2008, 64, 9828.
- [9] T. Rohand, E. Dolusic, T. H. Ngo, W. Maes, W. Dehaen, AR-KIVOC 2007, 10, 307.
- [10] J.-P. Strachan, D. F. O'Shea, T. Balasubramanian, J. S. Lindsey, J. Org. Chem. 2000, 65, 3150.
- [11] S. Szymański, P. Paluch, D. T. Gryko, A. Nowak-Król, W. Bocian, J. Sitkowski, B. Koszarna, J. Śniechowska, M. J. Potrzebowski, L. Kozerski, *Chem. Eur. J.* 2014, 20, 1720.
- [12] T. Ding, E. A. Alemán, D. A. Modarelli, C. J. Ziegler, J. Phys. Chem. A 2005, 109, 7411. In this paper, the fluorescence quantum yield of 4 was reported to be 0.14 with a reference of tetraphenylporphyrin ($\Phi_{\rm F} = 0.11$). However, the absolute quantum yield of 4 was determined with a Hamamatsu C9920–02S to be 0.060.
- [13] T. H. Ngo, F. Puntoriero, F. Nastasi, K. Robeyns, L. Van Meervelt, S. Campagna, W. Dehaen, W. Maes, *Chem. Eur. J.* 2010, 16, 5691.
- [14] J. Shen, J. Shao, Z. Ou, W. E. B. Koszarna, D. T. Gryko, K. M. Kadish, *Inorg. Chem.* 2006, 45, 2251.
- [15] a) T. Tanaka, S. Hayashi, M. Kitano, N. Aratani, A. Osuka, Org. Lett. 2012, 14, 2694; b) M. F. Bento, M. J. Medeiros, M. I. Montenegro, C. Beriot, D. Pletcher, J. Electroanal. Chem. 1993, 345, 273.

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A rational synthesis of cis-A₂B-type corroles through a [2+2] approach has been developed, which allowed the synthesis of six new corroles in moderate yields. These corroles were structurally well-characterized and their optical and electrochemical properties were also studied.



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