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Novel quinone-fused corroles

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Abstract—Gallium(III)(pyridine) complex of 5,10,15-tris(pentafluorophenyl)corrole-3-carbaldehyde was used as a precursor of an azomethine ylide, which was trapped in 1,3-dipolar cycloaddition reactions with quinones. Besides the expected dehydrogenated 1,3-dipolar cycloadducts, novel quinone-fused corrole derivatives were also obtained in moderate yields.
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1. Introduction

In the last decade, the corrole chemistry has attracted the interest of many researchers, mainly due to the disclosure of efficient synthetic methodologies[1] and their promising potential applications[2] in catalysis,[3] in the production of sensors[4] and solar cells[5] and also in medicine.[6] Knowing that the properties/activities of these compounds are strongly dependent on the structure of the substituents on the macrocycle, the chemical functionalization of corroles at the β- and *meso*-positions is an active and exciting field.[7]

In the past few years we have shown that porphyrins can participate in Diels–Alder[8] and in 1,3-dipolar cycloaddition[9] reactions. We have also reported that corroles take part in [4+2] and [4+4] cycloadditions.[10] Now we report the use of the gallium(III)(pyridine) complex of 5,10,15-tris(pentafluorophenyl)corrole-3-carbaldehyde[7c,11] **1** as a precursor of azomethine ylide **2** and its reaction with 1,4-benzoquinone, 1,4-naphthoquinone, and 1,4-anthraquinone. Besides the expected dehydrogenated 1,3-dipolar cycloadducts, novel quinone-fused corrole derivatives were also obtained (Scheme 1).

The first cycloaddition reaction was carried out by refluxing a toluene solution of corrole-3-carbaldehyde **1**, *N*-methylglycine (7 equiv), and 1,4-benzoquinone

(2 equiv) for 1 h.[12] TLC analysis of the reaction mixture revealed only one major product, which was purified by flash chromatography (silica); compound **3** (green) was obtained in 90% yield. Its ^{1}H NMR spectrum[13,14] shows one singlet at δ 9.18 ppm (H-2) and several doublets at δ 8.56–9.16 ppm corresponding to the other β-pyrrolic protons. The signals at δ 6.57, 6.76, 7.56 ppm were assigned to the resonances of the isoindole protons; the resonance of the N–CH$_3$ protons appears at δ 3.70 ppm. The HMBC spectrum shows correlation between the singlet at δ 9.18 ppm (H-2) and the signal at δ 133.5 ppm (C-1′), which is correlated with the singlet at δ 3.70 ppm (N–CH$_3$). This is consistent with the structure proposed for compound **3**.

Interestingly, the reaction with 1,4-naphthoquinone, under similar reaction conditions, afforded the expected compound **4**[15] (27% yield) and also the novel quinone-fused corrole derivative **5**[16] as the main product (46% yield). The formation of compound **5** is quite surprising since a similar reaction with a β-formylporphyrin, *N*-methylglycine, and 1,4-naphthoquinone only afforded the expected dehydrogenated 1,3-dipolar cycloadducts.[9b] This result shows a clear difference in the reactivity of porphyrins and corroles. The same type of quinone-fused corrole derivative was also obtained when 1,4-anthraquinone[17] was used as dipolarophile. In this case compounds **6**[18] and **7**[19] were obtained in 31% and 18% yields, respectively.

The structure of compounds **5** and **7** was deduced from their mass and NMR spectra. The mass spectrum of compound **5** shows a molecular ion peak at *m/z* 1042,
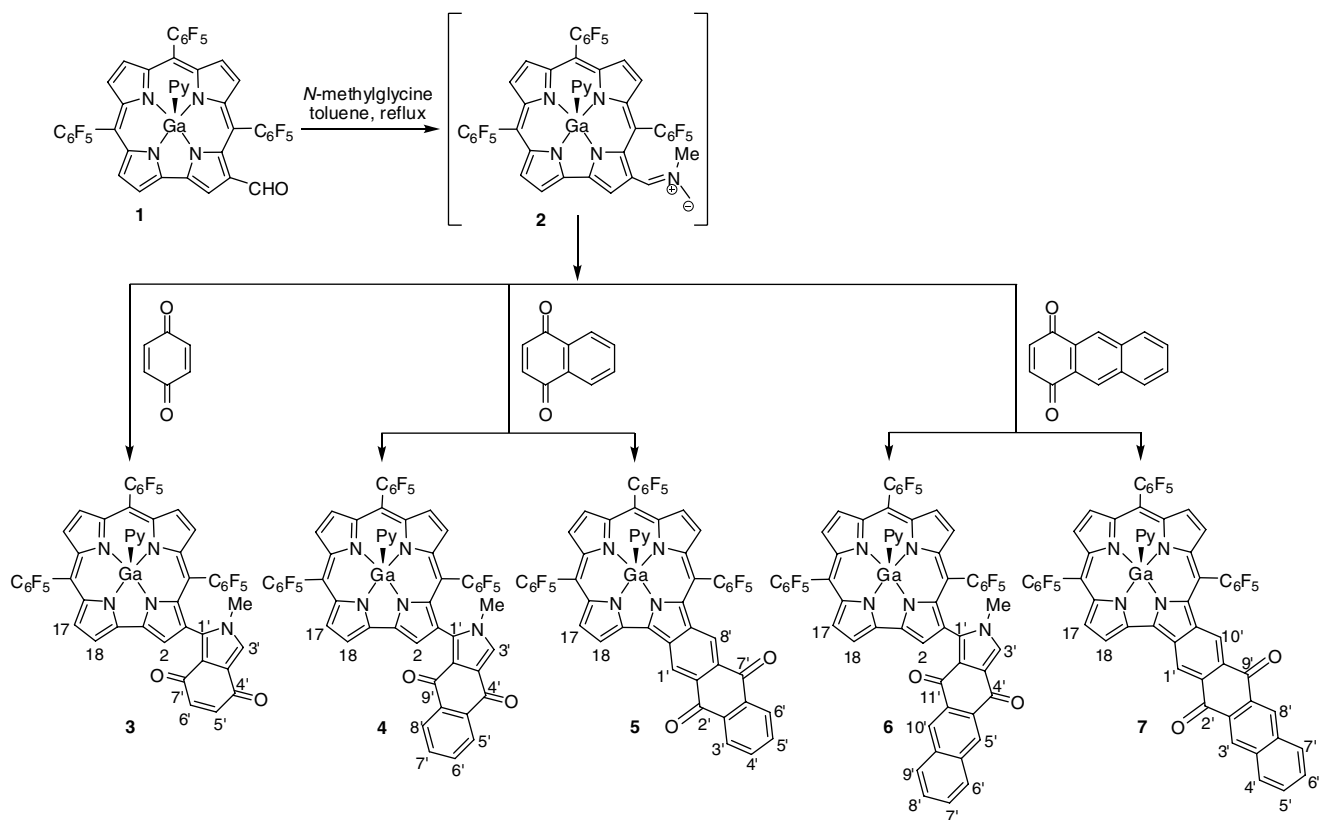
Scheme 1.

which corresponds to the molecular weight of the 1,3-dipolar cycloadduct minus a methylamine molecule. While the ^{1}H NMR spectrum of **4** shows the signals corresponding to the N–CH$_3$ (δ 3.79 ppm) and H-2 (δ 9.25 ppm) protons, these signals are absent in the ^{1}H NMR spectrum of **5**, which shows two singlets at δ 9.04 ppm (H-8′) and 10.32 (H-1′), eight doublets at δ 8.16–9.62 ppm and a multiplet at δ 7.57–7.62 ppm. The NOESY spectrum of **5** reveals a NOE cross-peak between the singlet at δ 10.32 ppm and the doublet at δ 9.62 ppm; the latter also couples with the doublet at δ 8.91 ppm. These three signals are due to the proton resonances of H-1′, H-18, and H-17, respectively. The HMBC shows correlations between the signal at δ 183.1 ppm of a carbonyl group and the signals of H-1′ and the doublet at δ 8.16 ppm. These signals were then assigned to the resonances of C-2′ and H-3′, respectively. The high chemical shift of H-18 is due to the deshielding anisotropic effect of the anthraquinone residue.

The structure of compound **5** was confirmed by single-crystal X-ray diffraction (Fig. 1).[20] The registered geometrical features of the derivatized 5,10,15-tris(pentafluorophenyl)corrolato ring are typical, as revealed by a search in the Cambridge Structural Database.[21,22] The first crystallographic report of a metallocorrole with Ga^{3+} was reported by Gross and co-workers.[7a]

The Ga–N bond lengths were found in the 1.943(13)–2.028(14) Å, which are in good agreement with those reported by Gross and co-workers for their compound. Nevertheless, it is interesting to note that the Ga^{3+} in **5**
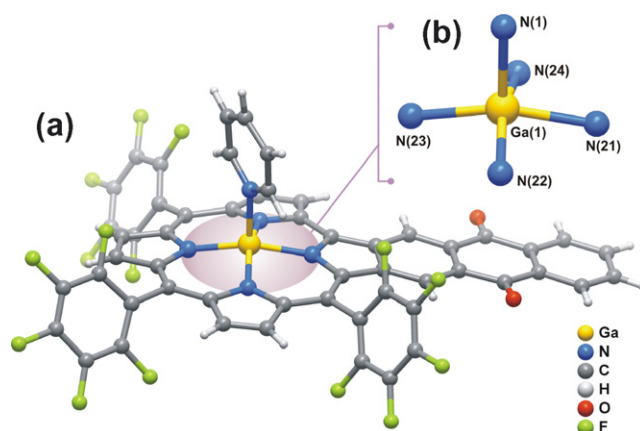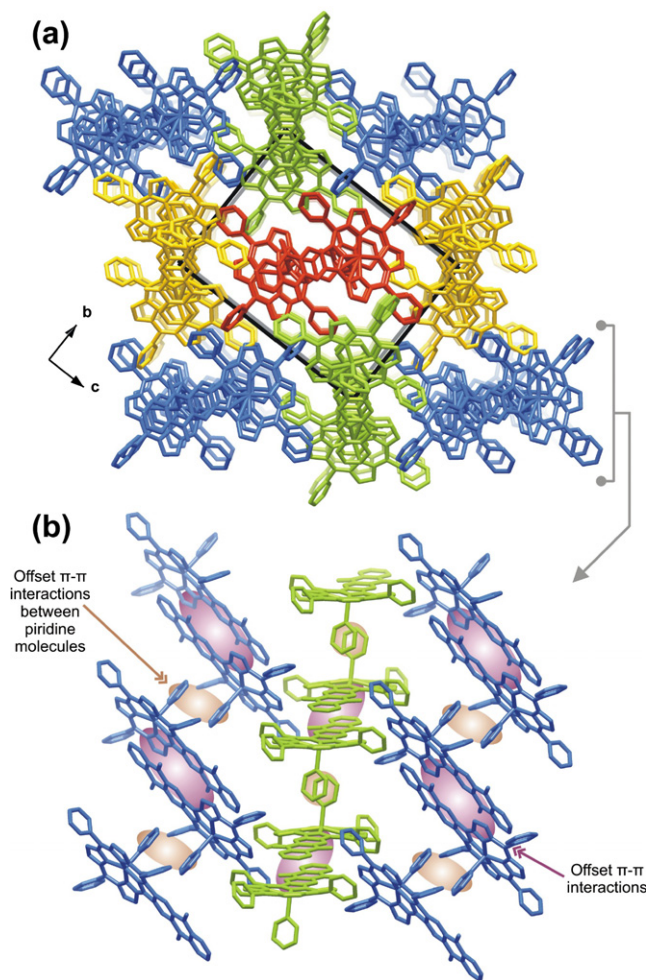

Figure 1. (a) Molecular unit present in the crystal structure of corrole **5**. (b) Detailed view of the coordination environment of the central Ga^{3+} cation, {GaN$_5$}, resembling a slightly distorted raised square pyramid. Bond lengths (in Å): Ga(1)–N(21) 1.977(13); Ga(1)–N(22) 1.946(14); Ga(1)–N(23) 1.943(13); Ga(1)–N(24) 1.957(13); Ga(1)–N(1) 2.028(14). Bond angles (in °): N(21)–Ga(1)–N(1) 99.9(6); N(22)–Ga(1)–N(21) 88.7(6); N(22)–Ga(1)–N(24) 157.5(5); N(22)–Ga(1)–N(1) 99.1(6); N(23)–Ga(1)–N(21) 157.3(5); N(23)–Ga(1)–N(22) 94.8(6); N(23)–Ga(1)–N(24) 89.1(6); N(23)–Ga(1)–N(1) 101.6(6); N(24)–Ga(1)–N(21) 79.6(6); N(24)–Ga(1)–N(1) 101.8(6).
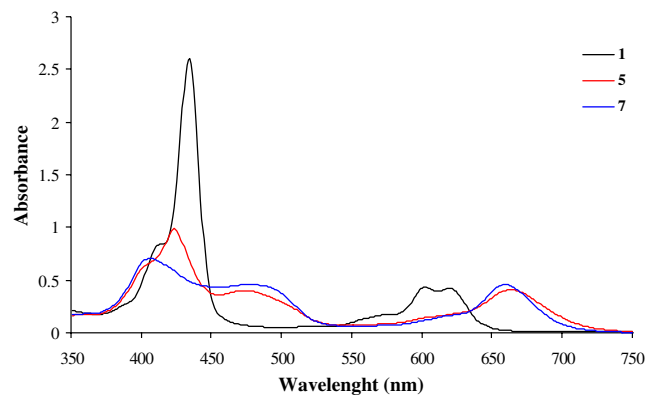
is raised from the basal plane by only ca. 0.36 Å, which is a statistically distinct value from that described by Gross and co-workers (average of about 0.41 Å). Individual molecular units of corrole **5** close pack along the [1 0 0] direction of the unit cell mediated by a series of cooperative π–π interactions, which alternate between

those involving the coordinated pyridine molecules (strengthened by C–H···π interactions—not shown), and those involving the derivatized 5,10,15-tris(pentafluorophenyl)corrolato rings, ultimately leading to supramolecular ladders, which are interlocked in the *bc* plane of the unit cell in a typical herringbone fashion (Fig. 2).

The mechanism for the formation of compounds **5** and **7** is still under investigation but probably it involves a 1,5-electrocyclization of the azomethine ylide[23] to a pyrrolo-[3,4-*b*]corrole followed by a Diels–Alder reaction with 1,4-naphthoquinone (or 1,4-anthraquinone). Deamination of the resulting Diels–Alder adducts leads to the quinone-fused corrole derivatives **5** or **7**. A similar mechanism was proposed by Smith and co-workers for the synthesis of benzoporphyrins from pyrrolo[3,4-*b*]-porphyrins.[24]

Figure 3. Electronic absorption spectra of compounds **1**, **5**, and **7** at the same concentration (1.6×10^{-5} M) in chloroform.

The electronic absorption spectra of compounds **3**, **4**, and **6** are quite similar to that of corrole-3-carbaldehyde **1**. However, the spectra of the two quinone-fused corrole derivatives, which are similar between them, are significantly different from the spectra of the other products (Fig. 3). Besides the Soret band, they show intense absorption bands at 450–520 nm and at 650–670 nm. This indicates that in compounds **5** and **7** the delocalization of the π-electrons throughout the corrole and quinone units results in a π-extended chromophore.

In conclusion, we have shown, for the first time, that corrole-3-carbaldehyde **1** can be used as a precursor of azomethine ylides that participate in 1,3-dipolar cyclo-addition reactions with quinones. In those reactions, besides the expected dehydrogenated cycloadducts, novel π-extended corrole derivatives are also formed. This is in sharp contrast with the reactivity of β-formylporphyrins under similar reaction conditions. The novel quinone-fused corrole derivatives show interesting electronic absorption spectra, with intense absorption bands at 650–670 nm and, because of that, are potential candidates as photosensitizers for PDT.

Figure 2. (**a**) Crystal packing of corrole **5** viewed in perspective along the [1 0 0] crystallographic direction, emphasising the presence of supramolecular ladders (assembled via a series of cooperative π–π interactions) which pack in a typical herringbone fashion in the *bc* plane of the unit cell (ladders represented with different colour). (**b**) Schematic representation of the interlocking of adjacent ladders. Hydrogen and fluorine atoms have been omitted for clarity purposes.

Acknowledgments

References and notes

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11. The gallium(III)(pyridine) complex of 5,10,15-tris(pentafluorophenyl)corrole-3-carbaldehyde was selected simply because the formylation of corrole is best carried out using the corresponding gallium(III)(pyridine) complex.[7d]

12. *General procedure*: To a solution of gallium(III)(pyridine) complex of 5,10,15-tris(pentafluorophenyl)corrole-3-carbaldehyde 1 (20 mg, 0.021 mmol) in dry toluene (5 ml) were added N-methylglycine (12.8 mg, 7 equiv) and the appropriate quinone (2 equiv). The reaction mixtures were heated at reflux for 1 h (for 1,4-benzoquinone) or 7 h (for naphthoquinone and anthraquinone). The products were purified by flash chromatography or preparative TLC (silica) using hexane/ethyl acetate/pyridine (15:5:0.1) as the eluent. The anthraquinone derivatives were purified by column chromatography on neutral alumina. All compounds were crystallized from CH_2Cl_2/hexane/pyridine (a few drops).

13. The NMR spectra of all synthesized compounds were run in $CDCl_3$ plus a few drops of C_5D_5N. The coordinated pyridine is thus exchanged by a deuterated pyridine.

14. *Spectroscopic data for compound* **3**: ¹H NMR ($CDCl_3$ + drops of C_5D_5N, 300.13 MHz) δ 3.70 (s, 3H, N–Me), 6.57 (d, 1H, $J = 10.4$ Hz, H-6′), 6.76 (d, 1H, $J = 10.4$ Hz, H-5′), 7.56 (s, 1H, H-3′), 8.56, 8.65, 8.72, 8.90 (4d, 4 × 1H, $J = 4.6$ Hz, H-β), 8.79 (d, 1H, $J = 4.6$ Hz, H-17), 9.16 (d, 1H, $J = 4.0$ Hz, H-18), 9.18 (s, 1H, H-2). ¹³C NMR ($CDCl_3$ + drops of C_5D_5N, 75.47 MHz) δ 34.8 (N–Me), 92.5, 97.0, 99.5 (C-5, C-10, C-15), 117.8 (C-18), 119.2 (C-2), 119.5 (C-7′a), 120.8 (C-3′a), 122.9 (t, C-3,5 of C_5D_5N, $J = 24.9$ Hz), 123.9 (C-β), 124.5 (C-3′), 124.8 (C-β), 125.6 (C-1), 125.7 (C-17), 127.6 (C-β), 127.9 (C-β), 132.9, 133.5 (C-1′), 135.3 (t, C-4 of C_5D_5N, $J = 24.8$ Hz), 136.5, 138.8 (C-5′), 140.0 (C-6′), 140.5, 141.6, 143.7, 143.9 (C-6, C-9, C-11, C-14), 149.0 (t, C-2,6 of C_5D_5N, $J = 27.3$ Hz), 180.5 (C-7′), 181.5 (C-4′). UV–vis ($CHCl_3$) λ_{max} (logε) 420 (5.34), 602 (4.40). HRMS-ESI m/z for $C_{46}H_{14}F_{15}GaN_5O_2$ [M+H]⁺ calcd 1022.0158, found 1022.0192.

15. *Spectroscopic data for compound* **4**: ¹H NMR ($CDCl_3$ + drops of C_5D_5N, 500.13 MHz), δ 3.79 (s, 3H, N–Me), 7.61–7.65 (m, 1H, H-7′ overlapped by H-4 of C_6H_5N), 7.71–7.74 (m, 1H, H-6′), 7.74 (s, 1H, H-3′), 7.97 (d, 1H, $J = 7.7$ Hz, H-8′), 8.37 (d, 1H, $J = 7.9$ Hz, H-5′), 8.53–8.55 (m, H-β overlapped by H-2,6 of C_6H_5N), 8.65 (d, 1H, $J = 4.5$ Hz, H-β), 8.69 (d, 1H, $J = 3.7$ Hz, H-β), 8.80 (d, 1H, $J = 3.9$ Hz, H-17), 8.91 (d, 1H, $J = 4.5$ Hz, H-β), 9.17 (d, 1H, $J = 3.9$ Hz, H-18), 9.25 (s, 1H, H-2). ¹³C NMR ($CDCl_3$ + drops of C_5D_5N, 125.77 MHz) δ 35.2 (N–Me), 92.8, 97.4, 99.6 (C-5, C-10, C-15), 118.0 (C-18), 119.4 (C-2), 121.2, 122.5 (C-3′a, C-9′a), 123.2 (t, C-3,5 of C_5D_5N, $J = 25.0$ Hz), 124.1 (C-β), 124.9 (C-β), 125.2 (C-3′), 125.8 (C-17), 126.5 (C-8′), 126.8, 126.9 (C-5′), 127.8 (C-β), 128.1 (C-β), 133.0 (C-6′), 133.1 (C-8′a), 133.3 (C-7′), 134.1 (C-1′), 134.9 (C-4′a), 135.6 (t, C-4 of C_5D_5N, $J = 24.8$ Hz), 136.7, 140.8, 141.8, 143.9, 144.1 (C-6, C-9, C-11, C-14), 149.3 (t, C-2,6 of C_5D_5N, $J = 27.2$ Hz), 178.9 (C-9′), 180.0 (C-4′). UV–vis ($CHCl_3$) λ_{max} (logε) 422 (4.78), 600 (4.02). HRMS-ESI m/z for $C_{50}H_{16}F_{15}GaN_5O_2$ [M+H]⁺ calcd 1072.0315, found 1072.0307.

16. *Spectroscopic data for compound* **5**: ¹H NMR ($CDCl_3$ + drops of C_5D_5N, 500.13 MHz,) δ 7.57–7.62 (m, 2H, H-4′ and H-5′), 8.16 (d, 1H, $J = 7.2$ Hz, H-3′), 8.23 (d, 1H, $J = 7.4$ Hz, H-6′), 8.59 (d, 1H, $J = 4.3$ Hz, H-β), 8.67 (d, 1H, $J = 4.4$ Hz, H-β), 8.80 (d, 1H, $J = 4.3$ Hz, H-β), 8.85 (d, 1H, $J = 4.4$ Hz, H-β), 8.91 (d, 1H, $J = 3.9$ Hz, H-17), 9.04 (s, 1H, H-8′), 9.62 (d, 1H, $J = 3.9$ Hz, H-18), 10.32 (s, 1H, H-1′). ¹³C NMR ($CDCl_3$ + drops of C_5D_5N, 75.47 MHz) δ 93.8, 96.1, 97.2 (C-5, C-10, C-15), 119.1 (C-18), 122.4 (C-8′), 123.0 (t, C-3,5 of C_5D_5N, $J = 24.9$ Hz and C-1′), 124.1 (C-β), 125.0 (C-β), 125.5 (C-17), 126.3 (C-β), 126.96, 127.00 (C-3′, C-6′), 127.4 (C-β), 129.3, 129.7, 131.2 (C-1), 132.5, 132.6 (C-16), 133.6, 133.7 (C-4′, C-5′), 134.0, 134.1 (C-2′a, C-6′a), 135.3 (t, C-4 of C_5D_5N, $J = 24.8$ Hz), 137.7 (C-19), 138.1, 141.2, 141.6, 142.2, 142.7 (C-6, C-9, C-11, C-14), 149.1 (t, C-2,6 of C_5D_5N, $J = 27.2$ Hz), 182.7 (C-8′), 183.1 (C-2′). UV–vis ($CHCl_3$) λ_{max} (logε) 422 (4.76), 473 (4.37), 663 (4.39). HRMS-ESI m/z for $C_{49}H_{12}F_{15}GaN_4O_2$ M·⁺ calcd 1041.9971, found 1041.9935.

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18. *Spectroscopic data for compound* **6**: ¹H NMR ($CDCl_3$ + drops of C_5D_5N, 300.13 MHz), δ 3.79 (s, 3H, N–Me), 7.53–7.64 (m, 2H, H-7′ and H-8′), 7.80 (s, 1H, H-3′), 7.90

(d, 1H, $J = 7.9$ Hz, H-9′), 8.11 (d, 1H, $J = 8.2$ Hz, H-6′), 8.50 (s, 1 H, H-10′), 8.54–8.55 (m, H-β overlapped by H-2,6 of C_6H_5N), 8.65 (d, 1H, $J = 4.7$ Hz, H-β), 8.68 (d, 1H, $J = 5.0$ Hz, H-β), 8.80 (d, 1H, $J = 4.0$ Hz, H-17), 8.90–8.92 (m, 1H, H-β), 8.91 (s, 1H, H-5′), 9.19 (dd, 1H, $J = 4.0$ and $J = 0.9$ Hz, H-18), 9.27 (d, 1H, $J = 0.9$ Hz, H-2). UV–vis ($CHCl_3$) λ_{max} (log ε) 423 (4.85), 602 (4.16). HRMS-ESI m/z for $C_{54}H_{18}F_{15}GaN_5O_2$ [M+H]$^+$ calcd 1122.0471, found 1122.0500.

19. *Spectroscopic data for compound* **7**: ^{1}H NMR (C_5D_5N, 300.13 MHz) δ 7.63–7.65 (m, 2H, H-5′ and H-6′), 8.12–8.18 (m, 2H, H-4′ and H-7′), 0.19 (s, 1H, H-3′), 9.21 (d, 1H, $J = 4.7$ Hz, H-β), 9.30 (s, 1H, H-8′), 9.32 (d, 1H, $J = 4.4$ Hz, H-β), 9.42–9.43 (m, 2H, 2 H-β), 9.45 (s, 1H, H-10′), 9.58 (d, 1H, $J = 4.4$ Hz, H-β), 9.65 (d, 1H, $J = 4.1$ Hz, H-18), 10.84 (s, 1H, H-1′). UV–vis ($CHCl_3$) λ_{max} (log ε) 406 (4.65), 480 (4.44), 663 (4.45). HRMS-ESI m/z for $C_{53}H_{15}F_{15}GaN_4O_2$ [M+H]$^+$ calcd 1093.0206, found 1093.0241.

20. *Crystal data*: $C_{54}H_{17}F_{15}GaN_5O_2$, $M = 1122.45$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 14.852(3)$ Å, $b = 15.593(3)$ Å, $c = 20.113(3)$ Å, $\beta = 91.316(8)°$, $V = 4656.7(13)$ Å^3, μ(Mo $K\alpha$) = 0.702 mm^{-1}, $D_c = 1.601$ g cm^{-3}, purple prisms with crystal size of $0.14 \times 0.14 \times 0.03$ mm^3. Of a total of 29,606 reflections collected, 7529 were independent ($R_{int} = 0.1318$). Final $R_1 = 0.1773$ [$I > 2\sigma(I)$] and $wR_2 = 0.4671$ (all data). Data completeness to theta = 25.35°, 88.3%. Crystallographic data (excluding structure factors) for the structure reported in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-654082. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, UK. Fax: +44 1223 336033. E-mail: deposit@ccdc.cam.ac.uk.

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