

Supplementary Material

Two-way chromic interconversion of 2,2'-biphenol-6,6'-diyl dication with 5*H*,10*H*-dioxapyrene or 9*H*,10*H*-4,5-dihydroxyphenanthrene: Concomitant two-proton or two-electron transfer accompanied by drastic structural changes

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A: Supplementary Figures

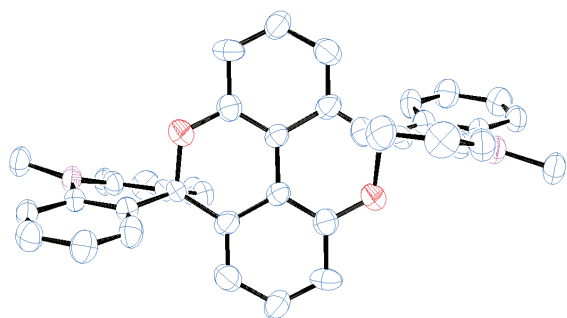
- Figure S1.** X-ray structure of **1**
Figure S2 X-ray structure of **2**²⁺ in **2**²⁺(BF₄⁻)₂ salt
Figure S3 X-ray structure of MOM-**2**²⁺ in MOM-**2**²⁺(BF₄⁻)₂(MeCN)_{0.5} salt
Figure S4 NMR titration of **1** to **2**²⁺
Figure S5 Halochromic response between **1** and **2**²⁺
Figure S6 Cyclic voltammograms of **2**²⁺(BF₄⁻)₂ salt and **3**

B: Experimental Details and Spectral Data of New Compounds

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Preparation of bis(hydroxy)base **6**
Preparation of dication salt **2**²⁺(BF₄⁻)₂
Preparation of dioxapyran **1**
Preparation of dihydrophenanthrene **3**

A: Supplementary Figures

a) top view



b) side view

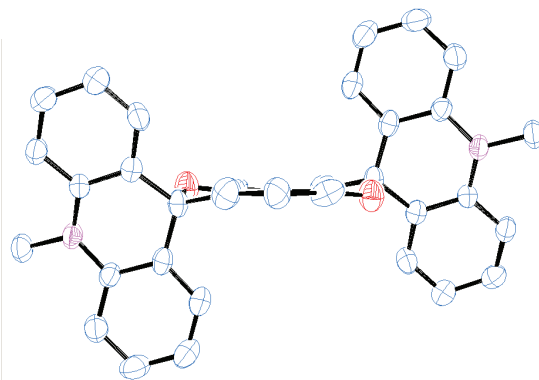
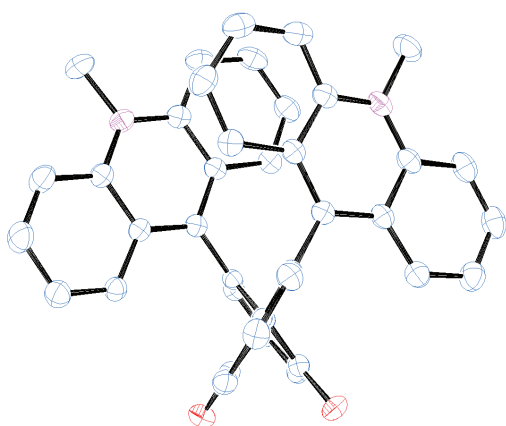


Figure S1. ORTEP drawings of **1** determined by X-ray analysis measured at 150 K [CCDC 1061368; crystal data: $a = 9.176(6)$, $b = 8.514(5)$, $c = 18.197(11)$ Å, $\beta = 104.0345(10)^\circ$, $V = 1379.2(15)$ Å³, $P21/c$, $Z = 2$].

a) top view



b) side view

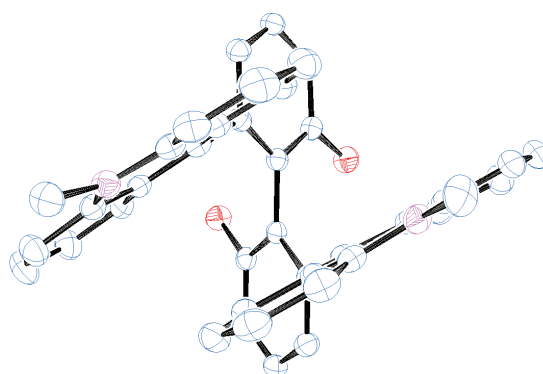
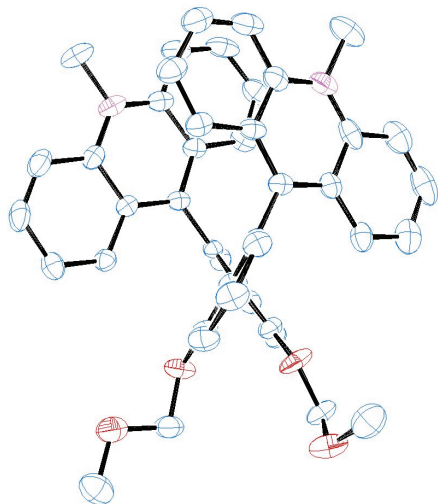
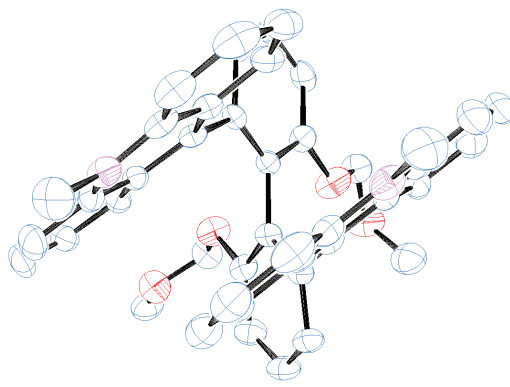


Figure S2. ORTEP drawings of **2²⁺** in **2²⁺(BF₄⁻)₂** salt determined by X-ray analysis at 150 K [CCDC 1061367; crystal data: $a = 12.1706(19)$, $b = 19.581(3)$, $c = 27.574(4)$ Å, $V = 6571.2(18)$ Å³, $Pbca$, $Z = 8$].

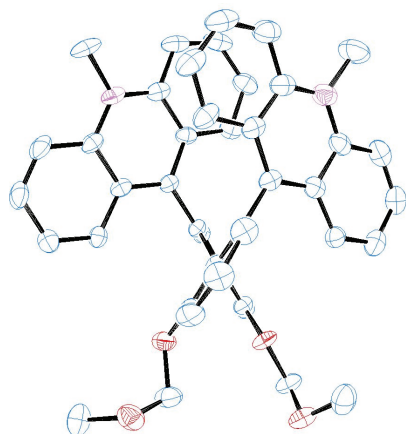
a) top view (mol-1)



b) side view (mol-1)



c) top view (mol-2)



d) side view (mol-2)

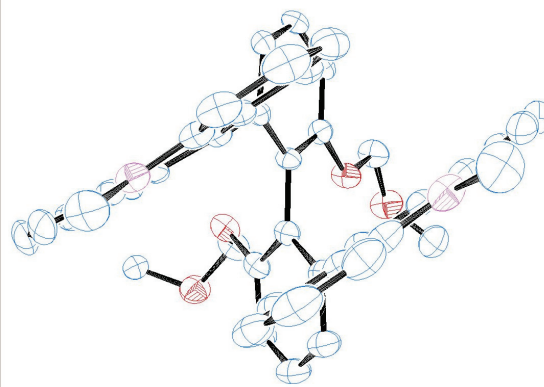


Figure S3. ORTEP drawings of MOM-2²⁺ in MOM-2²⁺(BF₄⁻)₂-(CH₃CN)_{0.5} salt determined by X-ray analysis measured at 150 K [CCDC 1061369; crystal data: a = 20.444(4), b = 13.566(3); c = 28.627(6) Å, β = 90.776(3)°, V = 7939(3) Å³, P21/c, Z = 8].

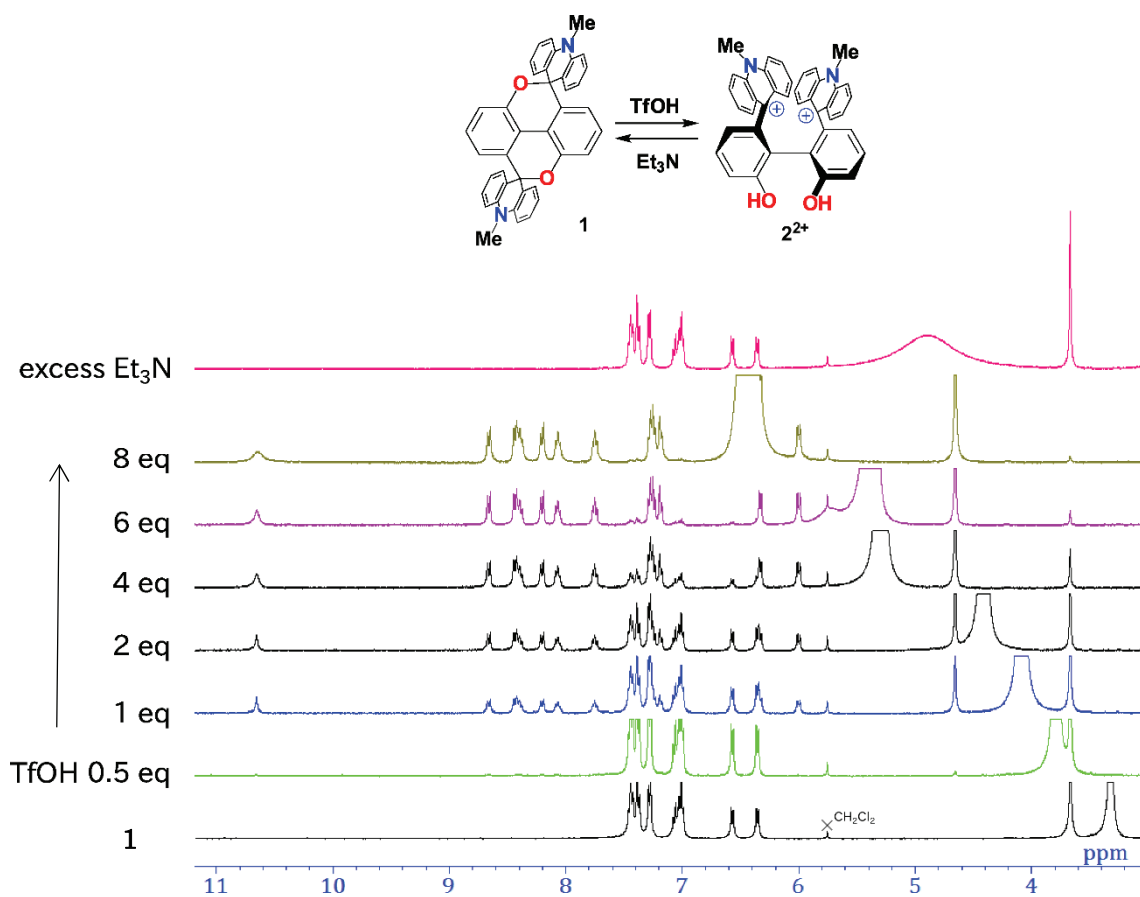


Figure S4. Changes in partial ¹H NMR spectra (3 -11 ppm) of **1** (8 mM) in DMSO-*d*₆ upon gradual addition of TfOH to transform into **2²⁺**. As-prepared **2²⁺** was then converted into **1** by addition of excess Et₃N.

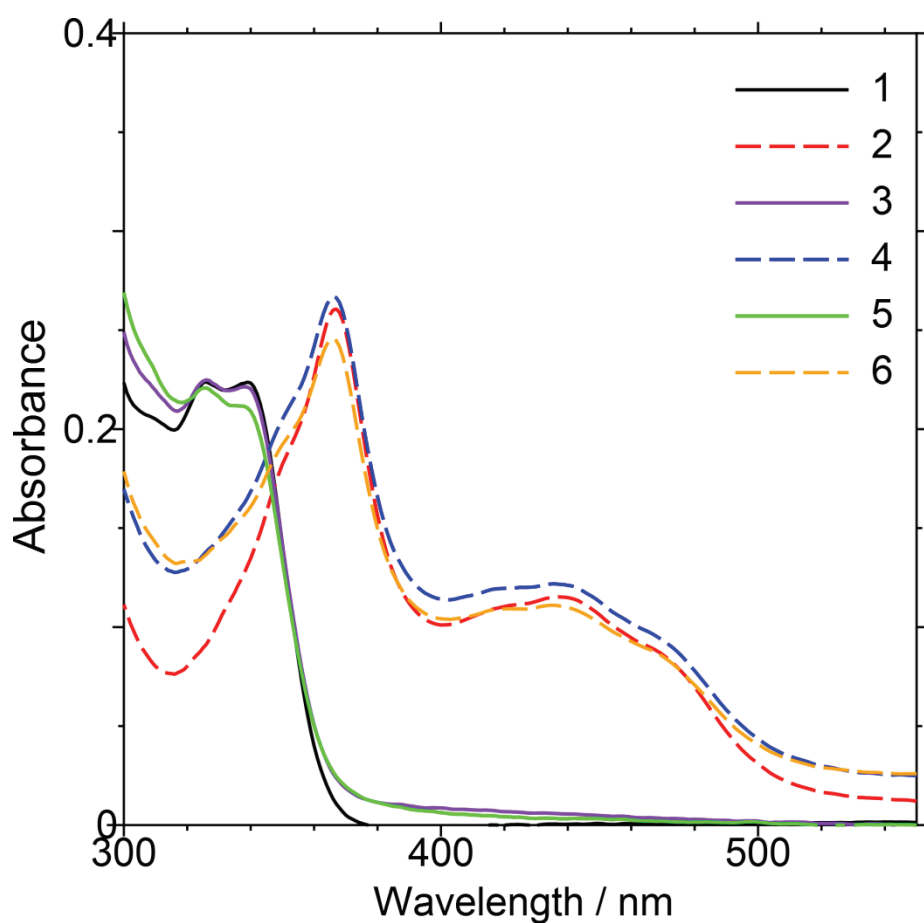


Figure S5. Reversible halochromic response between **1** and **2²⁺** (1.2×10^{-5} M in DMSO) upon repeated addition of TfOH (100 μ L) and Et₃N (200 μ L). Line-1: **1** before addition of acid; line-2: after addition of TfOH (100 μ L) to transform into **2²⁺**; line-3: after addition of Et₃N (200 μ L) to regenerate **1**; line-4: after further addition of TfOH (100 μ L) to transform into **2²⁺**; line-5: after further addition of Et₃N (200 μ L) to regenerate **1**; and line-6: after further addition of TfOH (100 μ L) to transform into **2²⁺**.

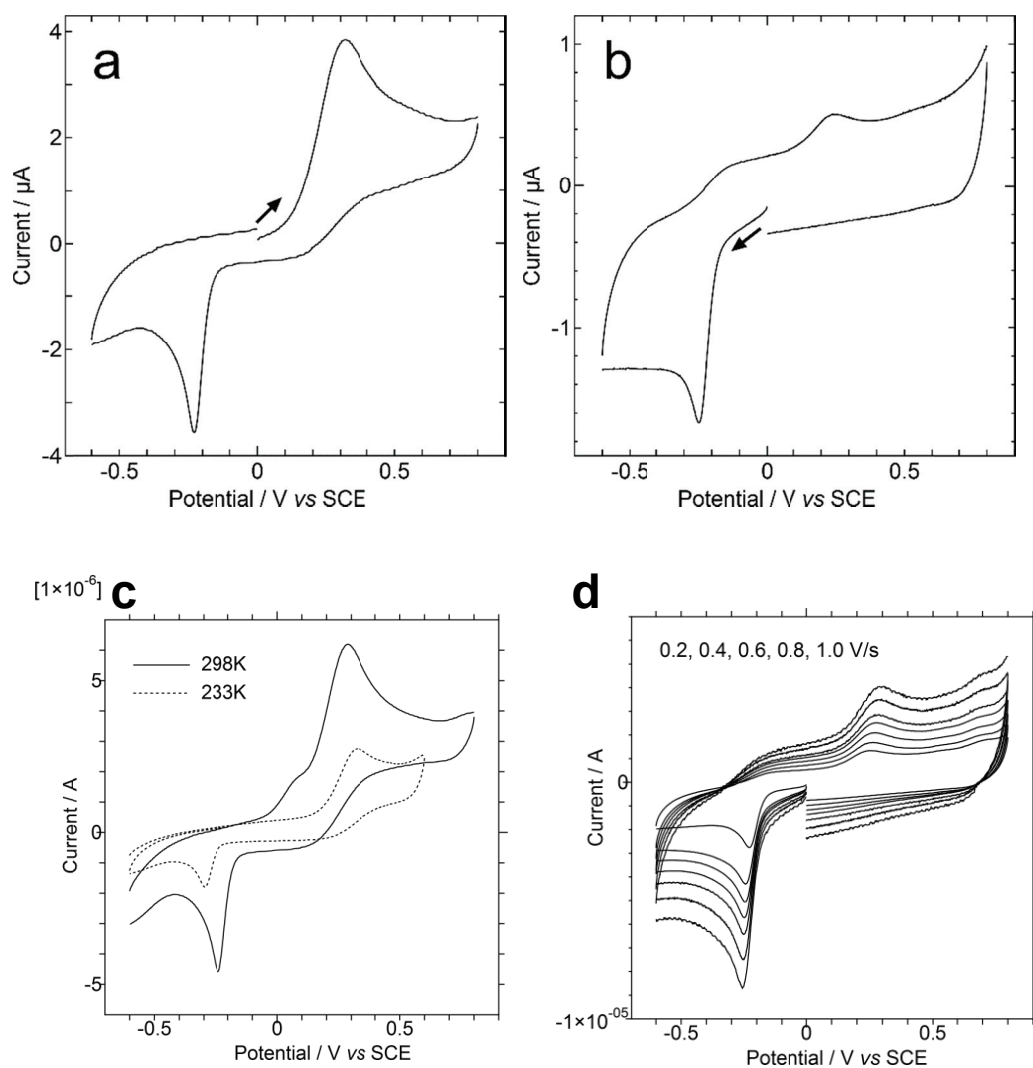
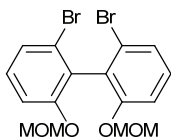


Figure S6. Cyclic voltammograms of (a) DHP **3** and (b) dication $2^{2+}(\text{BF}_4^-)_2$ in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (4:1) ($c = 0.5 \text{ mM}$) containing $0.1 \text{ M Bu}_4\text{NBF}_4$ (E/V vs. SCE, Pt electrode, scan rate 100 mV s^{-1} , 298K). To get some clue to the kinetics of conformational changes, the voltammogram of DHP **3** was also measured at lower temperature (233 K) (c). The voltammetry of dication $2^{2+}(\text{BF}_4^-)_2$ was also conducted at faster scan rates (100 mV s^{-1} - 1000 mV s^{-1}) (d). However, no drastic changes were observed under the conditions employed, suggesting that the conformational changes are rather fast processes.

B: Experimental Details and Spectral Data of New Compounds

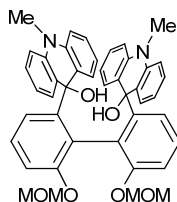
Preparation of bis(methoxymethyl) ether **5**



To a suspension of NaH (60% in oil, 1.27 g, 31.7 mmol) in dry DMF (20 mL) under argon was added a solution of 6,6'-dibromo-2,2'-biphenol **4** (2.73 g, 7.94 mmol) in dry DMF (20 mL) at 0 °C. After stirring for 10 min at ambient temperature, MOMCl (2.4 mL, 31.7 mmol) was added to the mixture. After stirring for 80 min at ambient temperature, water was added at 0 °C and the whole mixture was extracted with CH₂Cl₂ twice. The combined organic layer was washed with brine, dried over MgSO₄, and concentrated in vacuo. The residue was chromatographed on silica gel (hexane/CH₂Cl₂ = 2:3) to afford partially purified **5** (2.99 g). Further purification was conducted by recrystallization from EtOH to afford **5** (2.66 g, 77%) as a pale yellow solid.

mp: 156-157 °C. ¹H-NMR (400 MHz; CDCl₃): δ 7.32 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.20 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.15 (dd, *J* = 8.0, 1.3 Hz, 2H), 5.05 (d, *J* = 6.8 Hz, 2H), 5.03 (d, *J* = 6.8 Hz, 2H), 3.34 (s, 6H). ¹³C-NMR (101 MHz; CDCl₃): δ 155.7, 129.9, 129.2, 125.7, 125.1, 113.6, 94.7, 56.0 IR (KBr): 2996, 2957, 2941, 2908, 2849, 2830, 2797, 1584, 1569, 1485, 1451, 1442, 1409, 1402, 1306, 1261, 1248, 1206, 1184, 1163, 1157, 1142, 1092, 1084, 984, 921, 828, 772, 731, 669, 641, 564, 531, 426. FD-HRMS: *m/z* calcd for C₁₆H₁₆Br₂O₄ [M]⁺: 429.9415; found: 429.9415

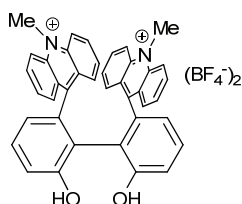
Preparation of bis(hydroxy)base 6



To a solution of **5** (800 mg, 1.85 mmol) in dry THF (25 mL) under argon was added *t*-BuLi (1.60 M in pentane, 4.6 mL, 7.41 mmol) at -78 °C. After stirring for 1 h at -78 °C, a suspension of *N*-methylacridone (774 mg, 3.70 mmol) in dry THF (25 mL) was added from a dropping funnel. After addition, the reaction mixture was warmed to ambient temperature and stirred for 21 h. Water was added and the organic solvents were removed in vacuo. The residue was extracted with EtOAc three times. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was chromatographed on silica gel (hexane/EtOAc = 4:1 containing 5% Et₃N) to afford **6** (904 mg, 70%) as a pale yellow solid.

mp: > 300 °C, ¹H-NMR (400 MHz; CDCl₃): δ 7.78 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.34 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 2H), 7.22 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 2H), 7.14 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.09 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.05 (dd, *J* = 8.2, 8.2 Hz, 2H), 7.01-6.97 (m, 4H), 6.94 (dd, *J* = 8.2, 1.0 Hz, 2H), 6.80-6.76 (m, 2H), 6.50 (dd, *J* = 8.0, 1.2 Hz, 2H), 4.75 (d, *J* = 6.5 Hz, 2H), 4.56 (d, *J* = 6.5 Hz, 2H), 3.85 (s, 2H), 3.51 (s, 6H), 3.19 (s, 6H). ¹³C-NMR (101 MHz; CDCl₃): δ 155.5, 142.5, 141.8, 141.1, 130.1, 129.2, 128.15, 128.10, 127.91, 127.88, 127.5, 126.8, 124.4, 120.4, 119.7, 112.7, 111.78, 111.71, 94.7, 55.7, 33.5. IR (KBr): 3373, 3060, 2883, 2821, 1735, 1593, 1572, 1499, 1468, 1402, 1347, 1308, 1270, 1246, 1199, 1151, 1131, 1076, 1030, 994, 956, 930, 920, 863, 820, 863, 820, 796, 750, 707, 647, 642. FD-HRMS: *m/z* calcd for C₄₄H₄₀N₂O₆ [M]⁺: 692.2886; found: 692.2880.

Preparation of dication salt $2^{2+}(\text{BF}_4^-)_2$

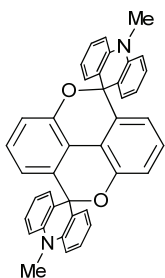


A mixture of diol **6** (216 mg, 0.311 mmol) and 42% HBF_4 aq. (1.0 mL, 6.3 mmol) in CHCl_3 (2.0 mL) and MeOH (2.0 mL) was heated at reflux for 1.5 h with stirring. After cooling, organic solvents were removed in vacuo. The remaining yellow precipitates were suspended in Et_2O and filtered to afford $2^{2+}(\text{BF}_4^-)_2$ (229 mg, 95%) as a yellow solid.

mp > 300 °C. $^1\text{H-NMR}$ (400 MHz; CD_3CN): δ 8.50 (d, $J = 9.2$ Hz, 2H), 8.45 (dd, $J = 8.6, 0.8$ Hz, 2H), 8.35 (ddd, $J = 9.2, 6.7, 1.2$ Hz, 2H), 8.14 (s, 2H), 8.08-8.02 (m, 4H), 7.82 (ddd, $J = 8.6, 6.7, 0.8$ Hz, 2H), 7.31 (dd, $J = 8.0, 8.0$ Hz, 2H), 7.23 (dd, $J = 8.2, 1.2$ Hz, 2H), 7.18-7.13 (m, 2H), 6.44 (dd, $J = 7.6, 1.2$ Hz, 2H), 6.27 (d, $J = 8.6$ Hz, 2H), 4.60 (s, 6H). $^{13}\text{C NMR}$ (101 MHz; CD_3CN): δ 159.8, 156.3, 140.66, 140.64, 139.0, 138.0, 133.4, 130.8, 129.5, 127.8, 127.4, 126.5, 125.9, 125.5, 125.0, 123.6, 118.5, 117.6, 38.5. IR (KBr): 3439, 3098, 1609, 1578, 1549, 1461, 1439, 1373, 1286, 1084, 1054, 851, 805, 767, 661, 602, 521. FD-LRMS: m/z 568 $[\text{M}-2\text{H}]^+$. Anal. Calc. for $\text{C}_{40}\text{H}_{30}\text{B}_2\text{F}_8\text{N}_2\text{O}_2$: C, 64.55; H, 4.06; N, 3.76. Found: C, 64.28; H, 4.17; N, 3.99%.

Upon oxidation of DHP **3** (*vide infra*), the dication salt of 2^{2+} was also obtained as follows. To a solution of **3** (104 mg, 0.182 mmol) in CH_2Cl_2 (5 mL) was added ferrocenium tetrafluoroborate (99 mg, 0.363 mmol). To the mixture was then added MeCN (5 mL). After stirred at ambient temperature for 20 min, the solvent was removed in vacuo. The residue was dissolved in MeCN (1.5 mL) and poured into Et_2O (50 mL). The precipitations were filtered to afford $2^{2+}(\text{BF}_4^-)_2$ (122 mg, 87%) as a yellow solid.

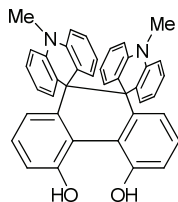
Preparation of dioxapyran **1**



To a solution of dication $\mathbf{2}^{2+}(\text{BF}_4^-)_2$ (136 mg, 0.176 mmol) in MeCN (10 mL) was added Et_3N (0.5 mL, 3.6 mmol). The precipitates were formed immediately. This solid was filtered and washed with MeCN to afford **1** (92 mg, 88%) as a colorless solid.

mp > 300 °C. $^1\text{H-NMR}$ (400 MHz; CDCl_3): δ 7.47-7.40 (m, 8H), 7.25-7.21 (m, 4H), 7.02-6.98 (m, 6H), 6.61 (dd, $J = 8.0, 0.9$ Hz, 2H), 6.49 (dd, $J = 8.0, 0.9$ Hz, 2H), 3.72 (s, 6H). $^{13}\text{C NMR}$ (101 MHz; CDCl_3): δ 148.7, 139.9, 133.8, 130.0, 129.23, 129.15, 124.5, 121.0, 120.0, 115.5, 114.6, 112.8, 80.2, 33.7. IR (KBr): 3069, 3034, 3008, 2960, 2895, 2828, 1595, 1575, 1472, 1438, 1360, 1263, 1182, 1168, 1131, 1105, 1051, 1012, 997, 903, 757, 747. FD-HRMS: m/z calcd for $\text{C}_{40}\text{H}_{28}\text{N}_2\text{O}_2$ $[\text{M}]^+$: 568.2151; found: 568.2150.

Preparation of dihydrophenanthrene 3



To a solution of dication $2^{2+}(\text{BF}_4^-)_2$ (150 mg, 0.194 mmol) in a mixture of 1 M HBF_4 aq. (0.5 mL) and MeCN (5.0 mL) under argon was added zinc dust (1.27 g, 19.4 mmol). After stirring for 2 h at ambient temperature, the reaction mixture was poured into a saturated NaHCO_3 aq. (40 mL) and extracted with EtOAc twice. The combined organic layer was washed with water and brine, dried over Na_2SO_4 , and concentrated in vacuo to afford **3** (105 mg, 95%) as a pale yellow solid.

mp > 300 °C. $^1\text{H-NMR}$ (400 MHz; CDCl_3 ; 240 K): δ 7.15-7.09 (m, 4H), 7.03-6.99 (m, 6H), 6.79 (dd, $J = 6.8, 2.2$ Hz, 2H), 6.59-6.55 (m, 4H), 6.45 (d, $J = 8.0$ Hz, 2H), 6.25-6.21 (m, 2H), 5.85 (d, $J = 7.6$ Hz, 2H), 2.70 (s, 6H). $^{13}\text{C NMR}$ (101 MHz; CDCl_3 ; 240 K): δ 150.1, 144.9, 144.0, 142.6, 133.0, 131.3, 128.5, 127.4, 126.5, 125.3, 124.7, 123.5, 119.4, 116.6, 116.4, 112.2, 110.1, 58.2, 34.2. IR (KBr): 2972, 2893, 1591, 1473, 1436, 1363, 1271, 1166, 1133, 1090, 1057, 1035, 863, 836, 788, 755, 728, 697, 658. FD-HRMS: m/z calcd for $\text{C}_{44}\text{H}_{30}\text{N}_2\text{O}_2$ $[\text{M}]^+$: 570.2307; found: 570.2308.