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Pyrazino-tetracyanonaphthoquinodimethanes: sterically deformed electron acceptors affording zwitterionic radicals

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Abstract—The X-ray analyses of the title electron acceptors (**1**) revealed their butterfly-shaped deformed geometry, which is not affected by the pyridyl group attached at 2-position of the pyrazino-TCNNQ skeleton. Small differences between the first and second reduction potentials (ca. 0.1 V) in pyrazino-TCNNQs show that their anion radicals ($\mathbf{1}^{-\cdot}$) are prone to disproportionate into the neutral (**1**) and dianionic ($\mathbf{1}^{2-}$) species. The thermodynamically unstable anion radical species based on the pyrazino-TCNNQ skeleton could be isolated as inner salts upon electrochemical reduction of the derivatives having an *N*-methylpyridinium moiety at 2-position ($\mathbf{2}^{+}$). The zwitterionic open-shell species ($\mathbf{2}^{\cdot}$) constitute a novel class of radicals that exhibit semiconducting behavior as a single component thanks to the high electrochemical amphotericity.

1. Introduction

7,7,8,8-Tetracyanoquinodimethane (TCNQ) has been known as a representative organic electron acceptor due to its strong oxidizing ability as well as stability of the negatively charged species. Many of its anion radical salts and charge-transfer complexes were proven highly conductive, and the discovery of the first organic metal[1] composed of TCNQ and tetrathiafulvalene (TTF) initiated the vast development of the research on organic conductors. While the TTF skeleton has been featured very often as an strong electron-donating moiety in materials science,[2] the chemistry of TCNQ has been less explored.[3–7] One of the reasons for this scarcity is the easy deformation of the skeleton by the steric hindrance between the Y-shaped dicyanomethylene groups and the substituents attached on the lateral C=C double bond, as exemplified by the severely non-planarized geometry of tetramethyl-TCNQ,[4] which no longer exhibits intrinsic redox properties of TCNQ. Accordingly, the π-extended analogs had to be designed with special care[5] in order to avoid steric factors[6] because simple benzannelation again induced butterfly-shaped deformation as shown by X-ray analyses of 11,11,12,12-tetracyanoanthraquinodimethanes (TCNAQs).[7] It seems the general view that the redox systems with a sterically deformed π-framework are inappropriate in developing organic solids with special properties such as electrical conductivity. That is, steric repulsion in neutral and/or charged species induces geometrical changes upon electron transfer,[8] thus decreasing the thermodynamic stability of ion radicals by easy disproportionation to the corresponding neutral and doubly-charged species.[9] On the contrary, when such unstable ion radicals could be isolated as salts, they provide a unique opportunity for further understanding of the physical properties of organic solids. Among the rare examples are the highly conductive cation radical salts of butterfly-shaped TTF derivatives, one of which exhibits metallic behavior.[10] With these in mind, we have decided to study on the anion radical species of the title electron acceptors with a non-planar geometry. The pyrazino-tetracyanonaphthoquinodimethanes (pyrazino-TCNNQs, **1**) are the 1,4-diaza derivatives of heavily deformed TCNAQ and were designed in anticipation of more flattened structure by partial reduction of the steric repulsion between dicyanomethylene groups and *peri*-hydrogens. It has been revealed in this study that the anion radicals of **1** could be successfully isolated when the pyridinium unit acting as a counter cation is attached on the periphery of the skeleton as in the inner salts $\mathbf{2Z}^{\cdot}$ (Scheme 1). They are new members of stable neutral radicals[11] with a polar structure.[12,13] Noteworthy is that radicals $\mathbf{2}^{\cdot}$ exhibit semiconducting behavior as a single

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Keywords: Redox system; Inner salt; Electron acceptor; Tetracyanoquinodimethane; Organic conductor; Deformation; Anion radical; Zwitterion.

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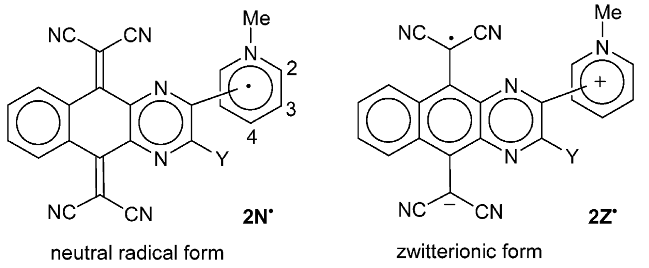


Scheme 1. Two forms of neutral radicals $2^{\cdot}$.

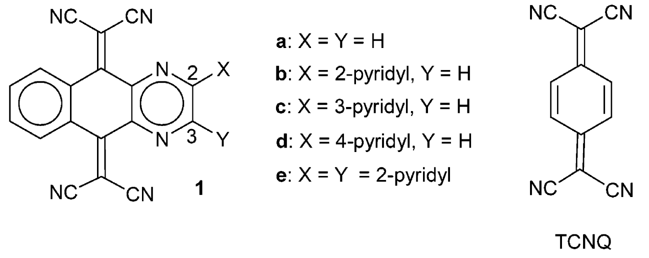


Chart 1.

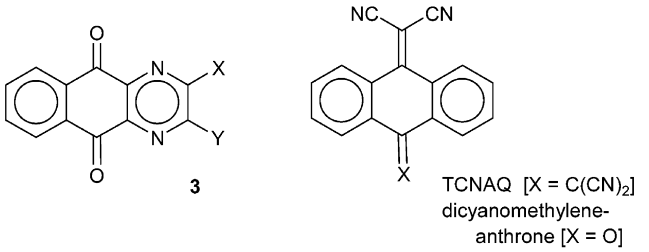


Chart 2.

component[12–14] thanks to the high electrochemical amphotericity (Charts 1 and 2).

2. Results and discussion

2.1. Preparation and molecular geometries of pyrazino-TCNNQs (1)

Condensation of pyrazino-naphthoquinones **3a-d** with malononitrile in the presence of $TiCl_4$[15] gave the corresponding naphthoquinodimethanes **1a-d** as slightly soluble yellow crystals.[16] The X-ray structural analysis of parent **1a** showed the butterfly-shaped deformation as expected (Fig. 1). The central six-membered ring adopts a boat-like conformation. The dihedral angle (α) defined by two fused aromatic rings is 148.0°, which is larger than those in TCNAQs (144.6° for parent;[7a] 143.3° for 2-chloro-TCNAQ[7b]) and rather close to the value in 9-dicyanomethyleneanthrone (152°).[17] Substituents on the fused pyrazine ring do not induce any significant structural change of pyrazino-TCNNQ skeleton, as shown by the quite similar molecular geometry of **1d** with a 4-pyridyl group at 2-position. Thus, not only the dihedral angle (α) but also the tilting (β) and twisting angles (γ) of exomethylene bonds are close to each other (Scheme 2). The pyridine pendant in **1d** lies nearly on the same plane to the fused pyrazine ring with a small torsion angle (δ) of 25.3°, which indicates the π-conjugation between the two nitrogen heterocycles.

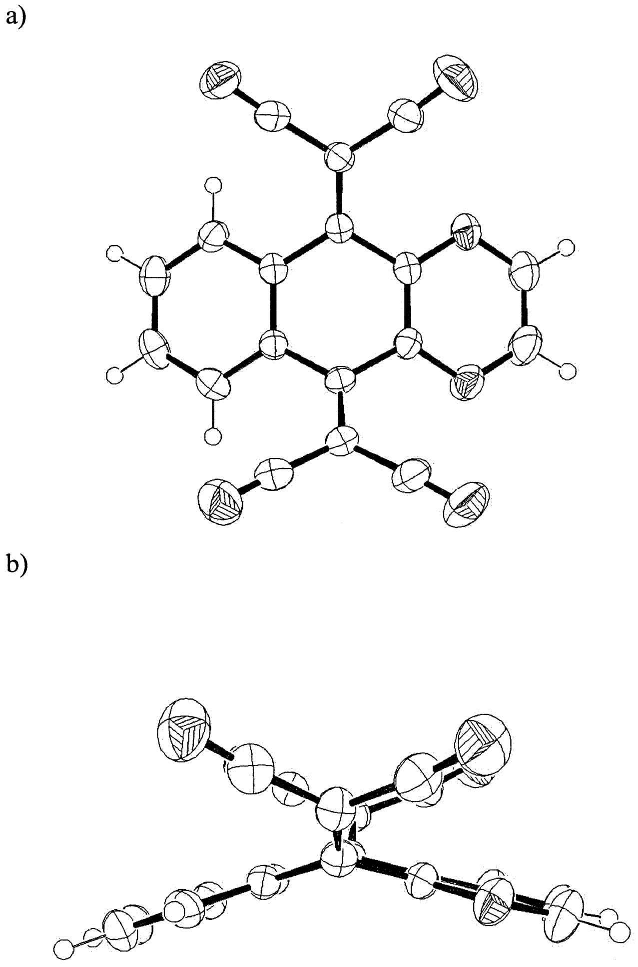
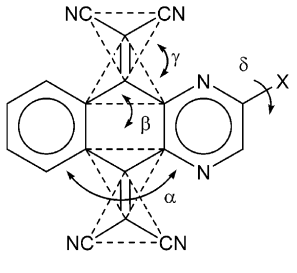


Figure 1. Molecular structure of **1a** determined by X-ray analysis: (a) top view; (b) side view.

2.2. Redox properties of pyrazino-TCNNQs (1) and quaternary cations (2^+)

In contrast to the one-wave two-electron reduction process observed in heavily deformed TCNAQ (E^{red}, −0.37 V vs. SCE), pyrazino-TCNNQ **1a** with a less deformed structure undergoes two-stage one-electron reduction. The first reduction potential (E_1^{red}, −0.23 V) is more positive than TCNAQ, indicating the higher electron-accepting properties due to the electron-withdrawing nature of a pyrazine ring



X	1a H	1d 4-py	2d$^+$ 1-Me-4-py$^+$
α (°)	148.0	148.9	152.8
β (°)	33.4 28.5	32.0 24.7	28.3 25.6
γ (°)	6.9 5.4	5.2 4.3	5.5 5.1
δ (°)	-	25.3	11.1

Scheme 2. Molecular geometries determined by X-ray analyses.

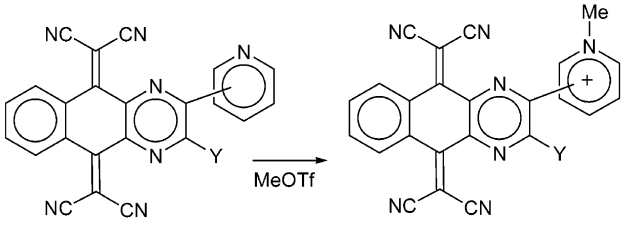
Table 1. Redox potentials of **1a-e** and **2b-e**$^+$ measured in MeCN[a]

	Substituent	E_1^{red}	E_2^{red}	E_3^{red}
1a	None	−0.23	−0.32	< −1.5
1b	2-(2-Pyridyl)	−0.20	−0.30	< −1.5
1c	2-(3-Pyridyl)	−0.19	−0.30	< −1.5
1d	2-(4-Pyridyl)	−0.19	−0.30	< −1.5
1e	2,3-(2-Pyridyl)	−0.18	−0.27	< −1.5
2b$^+$	2-(2-Pyridinium)	−0.12	−0.23	−1.03
2c$^+$	2-(3-Pyridinium)	−0.12	−0.24	−1.16
2d$^+$	2-(4-Pyridinium)	−0.13	−0.27	−0.96
2e$^+$	2-(2-Pyridinium)-3-(2-pyridyl)	−0.10	−0.22	−1.23

[a] E/V versus SCE, Pt electrode, scan rate 100 mV s^{-1}.

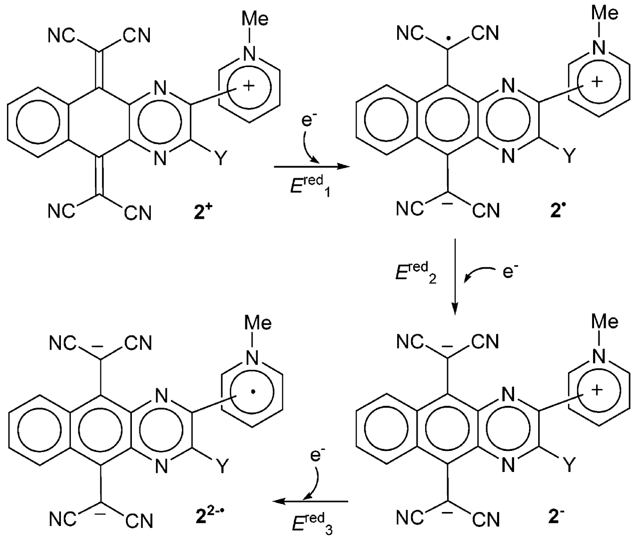
(Table 1). Although the two reduction peaks were observed separately in the cyclic voltammogram, the potential difference of ca. 0.1 V is much smaller than those of planar acceptors such as the corresponding quinone precursor **3a** (0.56 V) or TCNQ (0.54 V). The narrow separation corresponds to easy disproportionation of **1a**$^{-\bullet}$ to **1a** and **1a**$^{2-}$, as indicated by the small semiquinone formation constant (K_{sem}=[**1a**$^{-\bullet}$]^2/[**1**][**1a**$^{2-}$]=35).[18] Voltammograms of **1b-1d** with a pyridyl substituent as well as **1e**[13c] with two 2-pyridyl substituents at 2,3-positions are very similar to that of **1a**, showing the marginal electronic effects by the substituents on the redox behavior. However, considerable positive shifts of E_1^{red} and E_2^{red} were observed when the pyridine rings were converted to pyridinium groups with stronger electron withdrawing properties.

Quaternization of **1b-1e** with MeOTf resulted in the N-methylation at the pyridine pendant, and cations **2b**$^+$–**2e**$^+$ were isolated as pale yellow OTf$^-$ salts (Scheme 3). The X-ray analysis of the iodide salt of **2d**$^+$ showed that the molecular geometry of this cation resembles the neutral precursor **1d** (Scheme 2). Coplanarity of the pyridinium unit with the pyrazine ring (δ=11.1°) in **2d**$^+$ suggests full conjugation between the two nitrogen heterocycles, thus enhancing the electron-accepting properties of TCNNQ. In fact, cations **2**$^+$ are stronger oxidants than **1** and undergo two-stage one-electron reduction as in **1** (Table 1). Noteworthy is that cations **2**$^+$ undergo the third one-electron reduction process around −1 V, whose potential is close to E_1^{red} of N-methylpyridinium (−1.31 V). These results indicate that LUMO of **2**$^+$ mostly localizes on the pyrazino-TCNNQ skeleton, whereas the third electron is mainly accepted at the pyridinium unit (Scheme 4).



1b-e **2b-e**$^+$ OTf$^-$

Scheme 3. N-methylation of **1b-e** to cations **2b-e**$^+$.



Scheme 4. Multi-stage redox behavior of cations **2**$^+$.

2.3. Generation and properties of radicals (2$^{\bullet}$)

Electrochemical reduction of cations **2b**$^+$–**2e**$^+$ gave deeply colored solid which were assigned as the one-electron reduction products **2b**$^{\bullet}$–**2e**$^{\bullet}$. By considering that the similar electrolysis of **1a** did not afford its anion radical as a salt, coexistence of the counter cation within the pyrazino-TCNNQ skeleton plays an important role in isolating the anion radicals that undergo easy disproportionation.

The very low solubility of **2b**$^{\bullet}$–**2d**$^{\bullet}$ in common solvents prevents from examining their properties in solution. However, UV–vis spectrum of **2e**$^{\bullet}$ could be obtained in MeCN that exhibits absorptions in the longer-wavelength region [$\lambda_{\max}$ (log ε) 606 (4.00, sh) and 674 (4.22) nm] (Fig. 2). These bands are characteristic to the anion radical species of TCNQ derivatives, suggesting that the extra electron is mainly located at the TCNQ skeleton in **2**$^{\bullet}$. The CN stretching frequencies of **2**$^{\bullet}$ (2162–2167 cm^{-1}) were quite lower than those of the corresponding cationic precursors **2**$^+$ (2218–2220 cm^{-1}), indicating the delocalization of a negative charge over the dicyanomethylene moieties. These results suggest that the main contributor for the radicals **2**$^{\bullet}$ is the zwitterionic structure **2Z**$^{\bullet}$ but not the neutral radical form **2N**$^{\bullet}$ (Scheme 1) in consonant with the idea deduced from the redox potentials of cations **2**$^+$ (Scheme 4).

Many attempts to obtain single crystalline specimen of **2**$^{\bullet}$ were unsuccessful, thus lacking the experimental information on the detailed molecular structure of the radicals. However, the redox potentials of **2e**$^{\bullet}$ [E_1^{ox}=−0.10 V, E_1^{red}=−0.22 V, E_2^{red}=−1.23 V] clearly show that the radical is not dimeric but monomeric at least in solution. Thus,

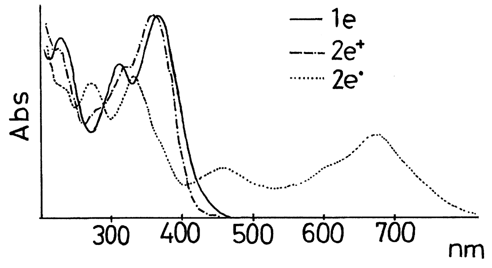


Figure 2. UV–vis spectra of **1e**, **2e**$^+$ and **2e**$^{\bullet}$ in MeCN.

these values correspond well to the reduction potentials (E_1^{red}, E_2^{red} and E_3^{red}) of the precursor $\mathbf{2e}^+$, respectively. Noteworthy is that the difference between E_1^{red} and E_2^{red} of $\mathbf{2}^+$ (ca. 0.1 V) is identical to the difference between E_1^{ox} and E_1^{red} (E_{sum}) of $\mathbf{2}^{\cdot}$. The E_{sum} value of ca. 0.1 V indicates very high electrochemical amphotericity of the resulted radicals $\mathbf{2}^{\cdot}$. There have been several papers reporting that highly amphoteric neutral radicals act as semiconductors as a single component,[12,13] and this is also the case. The electric conductivities of $\mathbf{2b}^{\cdot}$–$\mathbf{2e}^{\cdot}$ measured on the compaction samples by a two-probe method at room temperature are 8.4×10^{-8}, 2.1×10^{-7}, 9.0×10^{-8} and 2.0×10^{-6} S cm^{-1}, respectively. The values are not spectacular but comparable to those in other single-component organic semiconductor without any metal elements.[12b–c,14a–c] Furthermore, these radicals are ones of the rare examples[19] that sterically deformed electron acceptors afford organic conducting material.

3. Conclusion

This work has revealed that pyrazino-TCNNQs **1** with a sterically deformed geometry undergo reversible two-stage one-electron reduction. Although their anion-radicals $\mathbf{1}^{-\cdot}$ are thermodynamically unstable, they could be successfully isolated as inner salts $\mathbf{2}^{\cdot}$ by attaching the pyridinium unit acting as a counter cation within the molecule. This method provided a unique technique to study the solid-state properties of the ion radicals of pyrazino-TCNNQ that are otherwise unable to isolate.

4. Experimental

4.1. General

Melting points are uncorrected. Chemical shifts of ^{1}H NMR spectra are reported in ppm based on TMS (0 ppm). IR spectra were measured in KBr disks. Some compounds prepared here include solvent molecules (dichloroethane, acetonitrile, water) upon crystallization, which is rather common for non-planar molecules. Partial desolvation could be one of the reasons for the unsatisfactory analytical values (deviation >0.4%) observed in some compounds even after through purification. Another factor causing the disagreement is sensitivity toward moisture in the case of cations $\mathbf{2}^+$ and radicals $\mathbf{2}^{\cdot}$ due to their highly polar structures.

4.2. Preparation of pyrazino-TCNNQs (1)

4.2.1. 5,10-Bis(dicyanomethylidene)naphtho[2,3-*b*]pyrazine (1a).[16] To a solution of quinone **3a**[20] (400 mg, 1.90 mmol) in 40 mL of dry $CHCl_3$ was added $TiCl_4$ (0.8 mL, 7.3 mmol) under N_2. To the resultant suspension of the complex was then added dropwise a solution of malononitrile (400 mg, 6.1 mmol) and dry pyridine (6 mL, 50 mmol) in 20 mL of dry $CHCl_3$ over 2.3 h at −20 °C. After the entire mixture was stirred at this temperature for 3.5 h, it was poured into water and extracted with CH_2Cl_2. The combined extracts were washed with brine and dried over Na_2SO_4. Evaporation of solvent and chromatographic separation on SiO_2 (CH_2Cl_2/acetone, 10:1) followed by recrystallization from acetone–ether gave **1a** (77 mg) as yellow cubes in 13% yield: mp >260 °C decomp.; MS (EI) *m/z* (relative intensity) 306 (M$^+$, 100) and 252 (20); IR $\nu_{\max}$ 2216 (CN) cm^{-1}; UV–vis (MeCN) $\lambda_{\max}$ (log ε) 295 (4.05) and 350 (4.36) nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.89 (2H, s), 8.53–8.49 (2H, AA′BB′) and 7.90–7.85 (2H, AA′BB′). Anal. Calcd for $C_{18}H_6N_4$: C, 70.59; H, 1.97; N, 27.44. Found: C, 70.61; H, 1.73; N, 26.66.

4.2.2. 2-(2-Pyridyl)-5,10-bis(dicyanomethylidene)-naphtho[2,3-*b*]pyrazine (1b). To a solution of quinone **3b**[13c] (501 mg, 1.74 mmol) in 20 mL of dry CH_2Cl_2 was added $TiCl_4$ (1.15 mL, 10.5 mmol) under N_2. To the resultant suspension of the complex was then added dropwise a solution of malononitrile (692 mg, 10.5 mmol) and dry pyridine (2.5 mL, 30.9 mmol) in 50 mL of dry CH_2Cl_2 over 2.3 h at −78 °C. After the entire mixture was stirred at −20 °C for 4.5 h, it was poured into water and extracted with CH_2Cl_2. The combined extracts were washed with brine and dried over Na_2SO_4. Evaporation of solvent and chromatographic separation on SiO_2 (CH_2Cl_2) followed by recrystallization from 1,2-dichloroethane–MeOH gave **1b** (191 mg) as orange cubes in 29% yield. 3-Pyridyl (**1c**) and 4-pyridyl (**1d**) derivatives were obtained from the corresponding quinones[13c] by similar procedures to **1b**: mp 225–240 °C decomp.; MS (EI) *m/z* (relative intensity) 383 (M$^+$, 84), and 382 (100); IR $\nu_{\max}$ 2210 (CN) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 10.07 (1H, s), 8.88 (1H, ddd, *J*=4.7, 2.0, 1.2 Hz), 8.71 (1H, ddd, *J*=7.9, 1.2, 1.0 Hz), 8.58–8.54 (2H, m), 7.98 (1H, ddd, *J*=7.9, 7.8, 2.0 Hz), 7.89–7.84 (2H, m) and 7.50 (1H, ddd, *J*=7.8, 4.7, 1.2 Hz). Anal. Calcd for $C_{23}H_9N_7\cdot H_2O$: C, 68.83; H, 2.76; N, 24.43. Found: C, 68.86; H, 2.58; N, 24.21.

4.2.3. 2-(3-Pyridyl)-5,10-bis(dicyanomethylidene)-naphtho[2,3-*b*]pyrazine (1c). Yellow rods (yield 22%): mp 213–227 °C decomp.; MS (EI) *m/z* (relative intensity) 383 (M$^+$, 100), and 382 (62); IR $\nu_{\max}$ 2217 (CN) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.47 (1H, s), 9.45 (1H, dd, *J*=2.4, 0.9 Hz), 8.84 (1H, dd, *J*=4.9, 1.8 Hz), 8.72 (ddd, *J*=8.1, 2.4, 1.8 Hz), 8.59–8.53 (2H, m), 7.90–7.85 (2H, m) and 7.59 (1H, ddd, *J*=8.1, 4.9, 0.9 Hz). Anal. Calcd for $C_{23}H_9N_7\cdot0.25H_2O$: C, 71.22; H, 2.47; N, 25.28. Found: C, 71.57; H, 2.49; N, 25.17.

4.2.4. 2-(4-Pyridyl)-5,10-bis(dicyanomethylidene)-naphtho[2,3-*b*]pyrazine (1d). Yellow rods (yield 39%): mp 180–200 °C decomp.; MS (EI) *m/z* 383 (M$^+$); IR $\nu_{\max}$ 2218 (CN) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.48 (1H, s), 8.94–8.90 (2H, AA′XX′), 8.58–8.52 (2H, m), 8.18–8.15 (2H, AA′XX′) and 7.92–7.88 (2H, m). Anal. Calcd for $C_{23}H_9N_7\cdot0.75H_2O$: C, 69.61; H, 2.67; N, 24.70. Found: C, 69.87; H, 2.74 N, 24.43.

4.3. Preparation of quaternary salts ($\mathbf{2}^+$)

4.3.1. 1-Methyl-2-{5,10-bis(dicyanomethylidene)naphtho[2,3-*b*]pyrazin-2-yl}pyridinium triflate ($\mathbf{2c}^+\mathbf{OTf}^-$). To a hot solution of pyrazino-TCNNQ **1b** (41 mg, 0.11 mmol) in 12.5 mL of dry 1,2-dichloroethane was added MeOTf (60 μL, 0.53 mmol) under N_2. After the mixture was stirred for 4.5 h at 23 °C, filtration of the deposited precipitates gave **2b**$^+$OTf$^-$ as a pale yellow powder (10 mg) in 16% yield. 3-Pyridyl (**1c**) and 4-pyridyl (**1d**) derivatives were also converted to the corresponding quaternary salts by similar procedures to **2b**$^+$OTf$^-$: mp 183–190 °C decomp.; MS (FAB) *m/z* 398 (M$^+$); IR ν_{max} 2219 (CN) cm^{-1}; ^{1}H NMR (200 MHz, CD$_3$CN) δ 9.24 (1H, s), 8.87 (1H, dd, *J*=6.2, 1.8 Hz), 8.69 (1H, ddd, *J*=8.0, 7.9, 1.8 Hz), 8.54–8.47 (2H, m), 8.26 (1H, dd, *J*=8.0, 1.4 Hz), 8.19 (1H, ddd, *J*=7.9, 6.2, 1.4 Hz), 7.96–7.91 (2H, m) and 4.36 (3H, s). Anal. Calcd for $C_{25}H_{12}N_7F_3SO_3 \cdot 1.5H_2O$: C, 52.27; H, 2.63; N, 17.07. Found: C, 52.35; H, 2.35; N, 16.97.

4.3.2. 1-Methyl-3-{5,10-bis(dicyanomethylidene)naphtho[2,3-*b*]pyrazin-2-yl}pyridinium triflate (2c$^+$OTf$^-$).

A pale yellow powder (yield, 90%): mp 210–223 °C decomp.; MS (FAB) *m/z* 398 (M$^+$); IR ν_{max} 2220 (CN) cm^{-1}; ^{1}H NMR (200 MHz, CD$_3$CN) δ 9.56 (1H, s), 9.54 (1H, s), 9.29 (1H, dd, *J*=8.3, 1.4 Hz), 8.78 (1H, dd, *J*=6.2, 1.4 Hz), 8.57–8.50 (2H, m), 8.24 (1H, dd, *J*=8.3, 6.2 Hz), 7.95–7.90 (2H, m) and 4.42 (3H, s). Anal. Calcd for $C_{25}H_{12}N_7F_3SO_3 \cdot 1.5H_2O$: C, 52.27; H, 2.63; N, 17.07. Found: C, 52.67; H, 2.40; N, 16.85.

4.3.3. 1-Methyl-4-{5,10-bis(dicyanomethylidene)naphtho[2,3-*b*]pyrazin-2-yl}pyridinium triflate (2d$^+$OTf$^-$).

A pale yellow powder (yield, 88%): mp 167–200 °C decomp.; MS (FAB) m/z 398 (M+); IR ν_{max} 2218 (CN) cm^{-1}; ^{1}H NMR (200 MHz, CD$_3$CN) δ 9.65 (1H, s), 8.88–8.83 (2H, AA$'$BB$'$), 8.82–8.77 (2H, AA$'$BB$'$), 8.58–8.49 (2H, m), 7.96–7.91 (2H, m) and 4.36 (3H, s). Anal. Calcd for $C_{25}H_{12}N_7F_3SO_3 \cdot C_2H_4Cl_2$: C, 50.17; H, 2.50; N, 15.17. Found: C, 49.75; H, 2.40; N, 15.42.

4.3.4. 1-Methyl-2-{3-(2-pyridyl)-5,10-bis-(dicyanomethylidene)naphtho[2,3-*b*]pyrazin-2-yl}pyridinium triflate (2e$^+$OTf$^-$).

To a solution of 2,3-bis(2-pyridyl) substituted pyrazino-TCNNQ **1e**[13c] (103 mg, 0.224 mmol) in 20 mL of dry benzene was added MeOTf (25 mL, 0.22 mmol) in benzene (0.5 mL) under N$_2$. After the mixture was stirred for 2 h at 23 °C, filtration of the deposited precipitates gave **2e**$^+$OTf$^-$ as a pale yellow powder in 94% yield. When the reaction was conducted in CH$_2$Cl$_2$, by-production of bis(quaternary) salt made it difficult to isolate **2e**$^+$OTf$^-$: mp 173–187 °C decomp.; MS (FAB) *m/z* 475 (M$^+$); IR ν_{max} 2218 (CN) cm^{-1}; UV–vis (MeCN) λ_{max} (log ε) 194 (4.59), 222 (4.42), 282 (4.23, sh), 318 (4.36, sh) and 358 (4.50) nm; ^{1}H NMR (200 MHz, CD$_3$CN) δ 8.89 (1H, dd, *J*=6.3, 0.6 Hz), 8.69 (1H, ddd, *J*=7.9, 1.1, 1.0 Hz), 8.60–8.52 (2H, m), 8.21 (1H, ddd, *J*=4.8, 1.7, 1.0 Hz), 8.11 (1H, ddd, *J*=7.9, 6.3, 1.6 Hz), 8.01 (1H, ddd, *J*=7.9, 7.8, 1.7 Hz), 7.98–7.93 (2H, m), 7.80 (1H, dd, *J*=7.9, 1.6 Hz), 7.40 (1H, ddd, *J*=7.8, 4.8, 1.1 Hz) and 4.19 (3H, s). Anal. Calcd for $C_{30}H_{15}N_8F_3SO_3 \cdot 0.25H_2O$: C, 57.28; H, 2.48; N, 17.81. Found: C, 57.30; H, 2.60; N, 17.39.

4.4. Conversion of cations (2$^+$) to radicals (2$^{\cdot}$)

4.4.1. 1-Methyl-2-{5,10-bis(dicyanomethylidene)naphtho[2,3-*b*]pyrazin-2-yl}pyridyl (2b$^{\cdot}$).

The constant current electrochemical reduction (15 μA) of a solution of **2b**$^+$OTf$^-$ (24 mg, 0.043 mmol) in MeCN containing 0.05 mol dm^{-3} *n*Bu$_4$NBF$_4$ as a supporting electrolyte gave a black powder of low soluble radical **2b**$^{\cdot}$ (5 mg) in 29% yield. Cationic salts of **2d**$^+$OTf$^-$ and **2d**$^+$OTf$^-$ were also converted to the corresponding radicals by similar procedures to **2b**$^{\cdot}$: mp 293–302 °C decomp.; IR ν_{max} 2162 (CN) cm^{-1}. Anal. Calcd for $C_{24}H_{12}N_7 \cdot 1.5H_2O$: C, 67.76; H, 3.55; N, 23.05. Found: C, 67.74; H, 3.06; N, 23.38.

4.4.2. 1-Methyl-3-{5,10-bis(dicyanomethylidene)naphtho[2,3-*b*]pyrazin-2-yl}pyridyl (2c$^{\cdot}$).

A black powder (yield 25%): mp 223–226 °C decomp.; IR ν_{max} 2167 (CN) cm^{-1}. Anal. Calcd for $C_{24}H_{12}N_7 \cdot 2H_2O$: C, 66.36; H, 3.71; N, 22.57. Found: C, 66.70; H, 3.59; N, 21.78.

4.4.3. 1-Methyl-4-{5,10-bis(dicyanomethylidene)naphtho[2,3-*b*]pyrazin-2-yl}pyridyl (2d$^{\cdot}$).

A black powder (yield 65%): mp 220–265 °C decomp.; IR ν_{max} 2162 (CN) cm^{-1}. Anal. Calcd for $C_{24}H_{12}N_7 \cdot 2H_2O$: C, 66.36; H, 3.71; N, 22.57. Found: C, 66.58; H, 3.46; N, 22.16.

4.4.4. 1-Methyl-2-{3-(2-pyridyl)-5,10-bis(dicyanomethylidene)naphtho[2,3-*b*]pyrazin-2-yl}pyridyl (2e$^{\cdot}$).

The constant potential electrochemical reduction (−0.05 to −0.08 V vs. SCE) of a solution of **2e**$^+$OTf$^-$ (50 mg, 0.081 mmol) in CH$_2$Cl$_2$ containing 0.1 mol dm^{-3} *n*Bu$_4$NBF$_4$ as a supporting electrolyte gave dark blue fine needles of **2e**$^{\cdot}$ (29 mg) in 71% yield: mp 205–231 °C decomp.; IR ν_{max} 2163 (CN) cm^{-1}; UV–vis (MeCN) λ_{max} (log ε) 196 (4.67), 238 (4.41), 272 (4.42), 334 (4.45), 368 (4.20, sh), 462 (3.98), 606 (4.00, sh) and 674 (4.22) nm. Anal. Calcd for $C_{29}H_{15}N_8 \cdot 0.5H_2O$: C, 71.89; H, 3.72; N, 23.13. Found: C, 71.89; H, 3.48; N, 23.64.

4.5. Redox potential measurement

Redox potentials were measured by cyclic voltammetry in dry MeCN containing 0.1 mol dm^{-3} Et$_4$NClO$_4$ as a supporting electrolyte. Ferrocene undergoes one-electron oxidation at +0.38 V under the same conditions.

4.6. Crystallographic analyses

4.6.1. X-ray analysis of 1a.

Single crystalline yellow cubes were obtained by recrystallization from MeCN. Crystal data are as follows: $C_{18}H_6N_6$, *M* 306.29, triclinic, *P*1bar, *a*=7.231(1) Å, *b*=10.122(2) Å, *c*=11.133(2) Å, α=69.05(1)°, β=75.41(1)°, γ=72.00(1)°, *U*=714.5(2) Å^3, D_c (*Z*=2)=1.424 g cm^{-1}, μ=0.92 cm^{-1}. A total of 3160 unique reflection data (2θ<55°) were collected by a Rigaku AFC-7R diffractometer with a rotating anode (50 kV, 200 mA, Mo Kα, *T*=290 K) and a CCD camera. The structure was solved by the direct method, and non-hydrogen atoms were refined with the anisotropic temperature factors by the full-matrix least-squares method. Positions of hydrogen atom were calculated geometrically and verified by the electron density map. Their positions were not refined. The final *R* value is 0.036 for 1436 independent reflections with $I>1.5\sigma I$ and 217 parameters.

4.6.2. X-ray analysis of 1d.

Single crystalline yellow needles were obtained by recrystallization from CHCl$_3$. Crystal data are as follows: $C_{23}H_9N_7$, *M* 383.37, monoclinic, *P*21/*c*, *a*=9.887(3) Å, *b*=12.431(3) Å, *c*=15.367(4) Å, β=106.605(2)°, *U*=1809.9(8) Å^3, D_c (*Z*=4)=1.407 g cm^{-1}, μ=0.90 cm^{-1}. A total of 4110 unique reflection data ($2\theta<55°$) were collected by a Rigaku AFC-7R diffractometer with a rotating anode (50 kV, 200 mA, Mo Kα, T=290 K) and a CCD camera. The structure was solved by the direct method, and non-hydrogen atoms were refined with the anisotropic temperature factors by the full-matrix least-squares method. Positions of hydrogen atom were calculated geometrically and verified by the electron density map. Their positions were not refined. The final R value is 0.037 for 1607 independent reflections with $I>1.5\sigma I$ and 271 parameters.

4.6.3. X-ray analysis of 2d$^+$I$^-$·CH$_3$CN solvate. Single crystalline black needles were obtained by metathesis of **2d**$^+$OTf$^-$ and Et$_4$NI in MeCN in 88% yield: mp 135 °C decomp.; IR $\nu_{\max}$ 2218 (CN) cm^{-1}. Anal. Calcd for $C_{24}H_{12}N_7I\cdot CH_3CN$: C, 55.14; H, 2.67; N, 19.79. Found: C, 54.99; H, 2.87; N, 19.96. Crystal data are as follows: $C_{26}H_{15}N_8I$, M 566.37, triclinic, P1bar, a=10.269(3) Å, b=15.255(9)Å, c=9.186(3) Å, α=91.34(4)°, β=113.76(4)°, γ=92.93(4)°, U=1311.2(9) Å^3, D_c (Z=2)=1.435 g cm^{-1}, μ=12.336 cm^{-1}. A total of 5745 unique reflection data ($2\theta<55°$) were collected by a Rigaku AFC-5R four-circle diffractometer with a rotating anode (45 kV, 200 mA, Mo Kα, T=290 K). The structure was solved by the direct method, and non-hydrogen atoms were refined with the anisotropic temperature factors by the block-diagonal least-squares method. Hydrogen atoms were not included in the analysis. Positions of solvent molecules are disordered. The final R value is 0.068 for 4575 independent reflections with $I>3\sigma I$ and 344 parameters.

5. Supplementary Material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 219213 (**1a**), 219214 (**1d**), and 219608 (**2d**$^+$**I**$^-$ salt). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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