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One-Dimensional Single-Helix Coordination Polymers Self-assembled by Crown Ether Appended-N-Heteroacene Radical Anion

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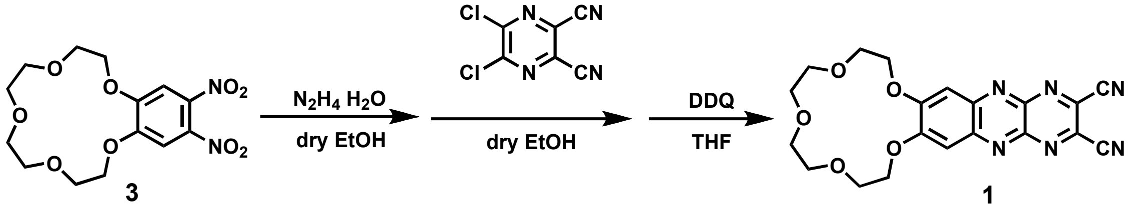
General Methods.

^{1}H and ^{13}C NMR spectra were recorded on a Varian UNITY INOVA400NB spectrometer. Chemical shift of ^{1}H and ^{13}C NMR signals were quoted to tetramethylsilane (δ = 0.00) and (δ = 77.00) as internal standards, respectively. FT-IR spectra were recorded with a Perkin-Elmer Spectrum Two FT-IR Spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were collected on a JEOL JMS-S3000 instrument using dithranol as a matrix. Elemental analyses were carried out with Perkin-Elmer instruments Series II CHNS/O Analyzer 2400II. Cyclic voltammetry was carried out in CH_3CN solutions (5 or 10 mL) of compounds (2.0 mM) and Bu_4NPF_4 (0.10 M) as electrolyte with glassy carbon working, Pt counter, and an Ag/Ag$^+$ reference electrode using an ALS CHI 600E electrochemical analyzer. UV-Vis-NIR absorption spectra were recorded with a SHIMADZU SolidSpec-3700 UV-Vis-NIR Spectrophotometer. Electron spin resonance (ESR) spectra were recorded with JEOL JES-FA200 spectrometer for **2** with sodium cations at r.t. and with FA-100 spectrometer equipped with an ESR900 cryostat (Oxford) for solutions fused in quartz tubes (for **1**, $NaBPh_4$, and both **1** and $NaBPh_4$). Single crystals for X-ray diffraction were grown from $CHCl_3$/hexane solution for **1** (See Experimental Section for **2**). A suitable single crystal was selected in Paratone® N oil at ambient temperature and mounted on a MiTeGen MicroMount™ using the oil. All diffraction data were collected at −173 °C on a Bruker Apex II Ultra X-ray diffractometer equipped with a Mo Kα radiation (λ = 0.71073) source. Intensity data were processed using the APEX3 software. The solution of the structures and the corresponding refinements were carried out using the Yadokari-XG[1] graphical interface. The positions of non-hydrogen atoms were determined by a dual-space method using the SHELXT-2014/5[2] program and refined on F^2 by full-matrix least-squares techniques using the SHELXL-2018/3[3] program. All non-hydrogen atoms were refined with anisotropic thermal parameters, while all the hydrogen atoms were placed using AFIX instructions. For **Na1**, although a residual peak slightly above 1 e/Å^3 was observed in the final difference map (Alert level C), no discrete and reliable solvent or small molecules could not be located at the position.



Scheme S1. Synthesis of **1**.

Synthesis of **2,3-dicyano-7,10,13,16,19-pentaoxacyclopentadecino[2,3-*g*]pyrazino[2,3-*b*]quinoxaline (1)**

To the suspension of **3** (1.8 g, 5.0 mmol) and Pd/C (0.5 g) in dry EtOH (150 ml) was slowly added dropwise $N_2H_4{\cdot}H_2O$ (5 ml) at 0 ˚C and then heated at 80 ˚C for 4 h under Ar. The reaction mixture was cooled to r.t. and filtrated through Celite under Ar. The reaction crude was heated with 1,2-dichloro,4,5-dicyanopyradine (1.0 g, 5.0 mmol) in dry EtOH (70 ml) at 80 ˚C for 24 h. After cooling to r.t., the product was filtrated and dried under vacuum. The obtained red solid was treated with DDQ (1.59 g, 7.0 mmol) for 2 h at r.t., and then the reaction mixture was extracted with $CHCl_3$ three times. The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by column chromatography (silica, $CHCl_3$/MeOH = 10/1 (v/v)), recrystallized with $CHCl_3$/hexane, and dried under vacuum to afford **1** as an orangish solid (0.80 g, 38%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 2H), 4.44 (t, J = 4.0 Hz, 4H), 4.05 (t, J = 4.0 Hz, 4H), 3.82 (m, 8H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.09, 142.61, 138.32, 131.86, 113.06, 105.37, 71.07, 69.82, 69.55, 68.19 ppm; MALDI-TOF-MS: m/z calcd: 422.39 $[M]^+$; found: 422.23; elemental analysis: calcd (%) for CHNO: C 56.87, H 4.30, N 19.90; found: C 56.52, H 4.35, N 19.67.

Electro-crystallization of radical anion 2·with Na$^+$

The solution of **1** (6.33 mg, 0.015 mmol) and $NaBPh_4$ (51.3 mg, 0.15 mmol) as electrolyte in dry CH_3CN (10 ml) was electro-crystallized upon the constant current of 2 μA for 3 days in N_2

atmosphere in glove box. The product was obtained as dark green solid. Table S1 shows various conditions to prepare the single crystal **2**.

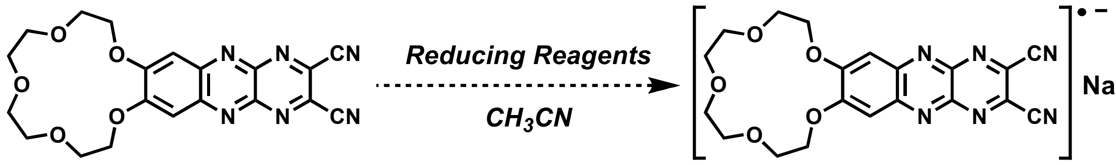
Table S1. Experiments for preparation of **2** in various conditions

No.	mmol	**1** : $NaBPh_4$(mmol)	μA[b]	Product
1	0.005	1:10	2	powder
2	0.010	1:5	2	powder
3	0.010	1:10	2	powder
4	0.010	1:15	2	powder
5	0.010	1:20	2	powder
6	0.015	1:10	1	powder
7	0.015	1:10	2	crystal [c]
8	0.015	1:100	1	powder
9	0.015	1:100	2	crystal
10	0.020	1:10	1	powder
11	0.020	1:10	2	crystal
12	0.020	1:50	2	crystal
13	0.030	1:100	1	powder
14	0.030	1:100	2	powder

a : solvent: dry CH_3CN(10 ml), electro-crystallized under Ar

b : applied constant current

c : analyzed by single-crystallographic X-ray analysis



1 / Neutral

2 / Radical Anion

Scheme S2. Synthesis of **1**.

Attempts to prepare 2 with Na^+

Na metal, NaH, or $NaBH_4$ (equimolar to **1**) was added slowly dropwise to the solution of **1** (4 mg) in CH_3CN (10 mL) at 0 ˚C under Ar atmosphere. The addition of Na metal and NaH immediately changed the color of CH_3CN solution of **1** from brown to green. In the case of Na metal and NaH, we obtained a little amount of dark-green powder, which was presumably radical anion **2**, however, we did not obtain single crystal to analysis the structures in detail. In contrast, the addition of $NaBH_4$ did not generate the precipitate despite the color change was observed.

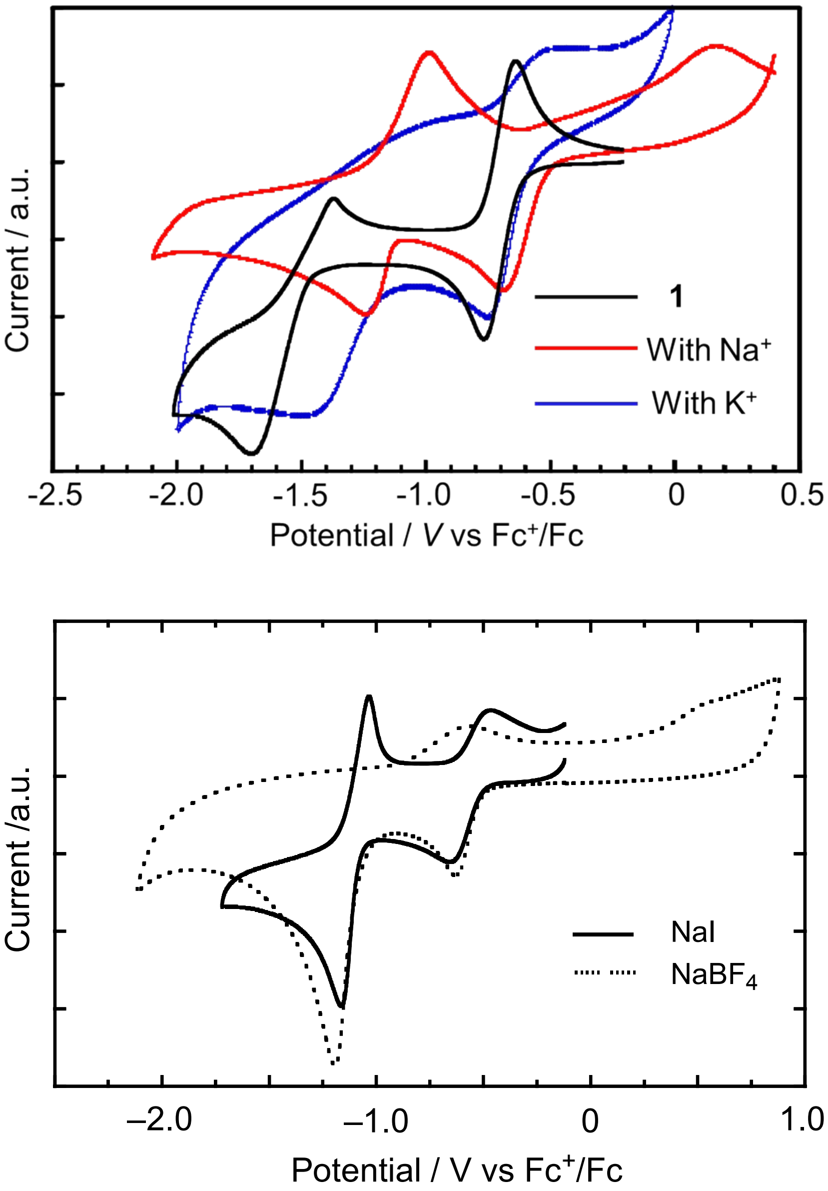


Figure S1. Cyclic voltammetry measurements of **1** in the presence/absence of $NaBPh_4$ and $KBPh_4$ (top) and **1** with NaI and $NaBF_4$ (10 eq. relative to **1**) (bottom) in CH_3CN solutions.

Table S2. Electrochemical data of **1** and **1** with $NaBPh_4$ and $KBPh_4$.

	E^1_{red}	E^2_{red}	ΔE^1_{red}	ΔE^2_{red}
1	–0.78	–1.70	–	–
1 + $NaBPh_4$	–0.68	–1.24	0.10	0.46
2 + $KBPh_4$	–0.74	–1.44	0.04	0.26

Figure S2. Photograph of setup for electrocrystallization of **1** with $NaBPh_4$ in a CH_3CN solution.

Table S3. Crystal data and structure refinement for **1** (ydkr_a) and **2** with sodium cation (Isoda1)

Identification code	ydkr_a	Isoda1
CCDC	1908846	1908847
Empirical formula	$C_{20}H_{18}N_6O_5$	$C_{20}H_{18}N_6NaO_5$
Formula weight	422.40	445.39
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	*Monoclinic*	*Monoclinic*
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 15.311(2) Å α = 90°. b = 14.370(2) Å β = 91.020(2)°. c = 8.7464(13) Å γ = 90°.	a = 15.823(6) Å α = 90°. b = 7.751(3) Å β = 97.807(6)°. c = 16.592(7) Å γ = 90°.
Volume	1924.0(5) Å^3	2016.0(14) Å^3
Z	4	4
Density (calculated)	1.458 mg/m^3	1.467 mg/m^3
Absorption coefficient	0.108 mm^{-1}	0.126 mm^{-1}
F(000)	880	924
Crystal size	0.137 × 0.051 × 0.037 mm^3	0.200 × 0.090 × 0.030 mm^3
Theta range for data collection	1.330 to 27.500°.	1.299 to 27.494°.
Index ranges	−19<=h<=19, −18<=k<=18, −11<=l<=11	−16<=h<=20, −10<=k<=9, −21<=l<=15
Reflections collected	21125	10720
Independent reflections	4395 [R(int) = 0.0413]	4485 [R(int) = 0.0724]
Completeness to theta = 25.242°	100 %	99.6 %
Data / restraints / parameters	4395 / 0 / 280	4485 / 0 / 289
Goodness-of-fit on F^2	1.018	1.020
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0376, wR_2 = 0.0812	R_1 = 0.0597, wR_2 = 0.1440
R indices (all data)	R_1 = 0.0576, wR_2 = 0.0904	R_1 = 0.1188, wR_2 = 0.1750
Largest diff. peak and hole	0.229 and −0.246 e.Å^{-3}	1.048 and −0.282 e.Å^{-3}

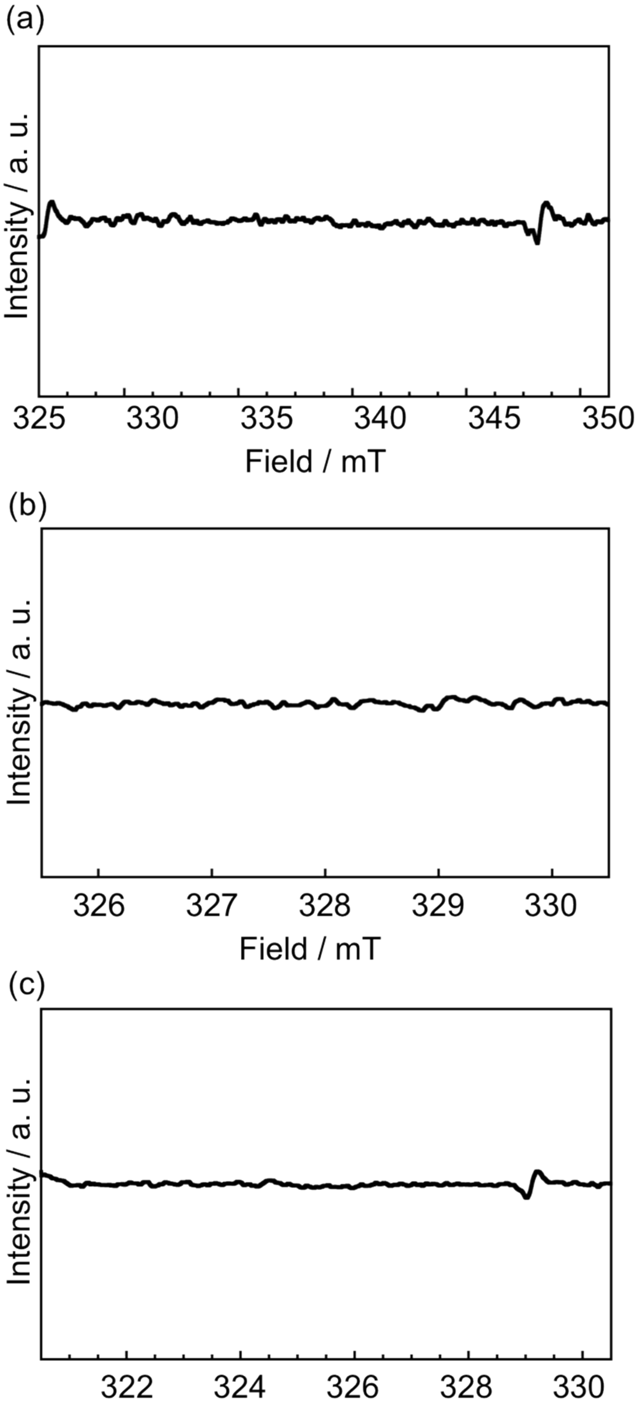


Figure S3. ESR spectrum of (a) **1** in a solid state and (b) **1** in a CH_3CN solution and (c) $NaBPh_4$ in a CH_3CN solution at –196 ˚C.

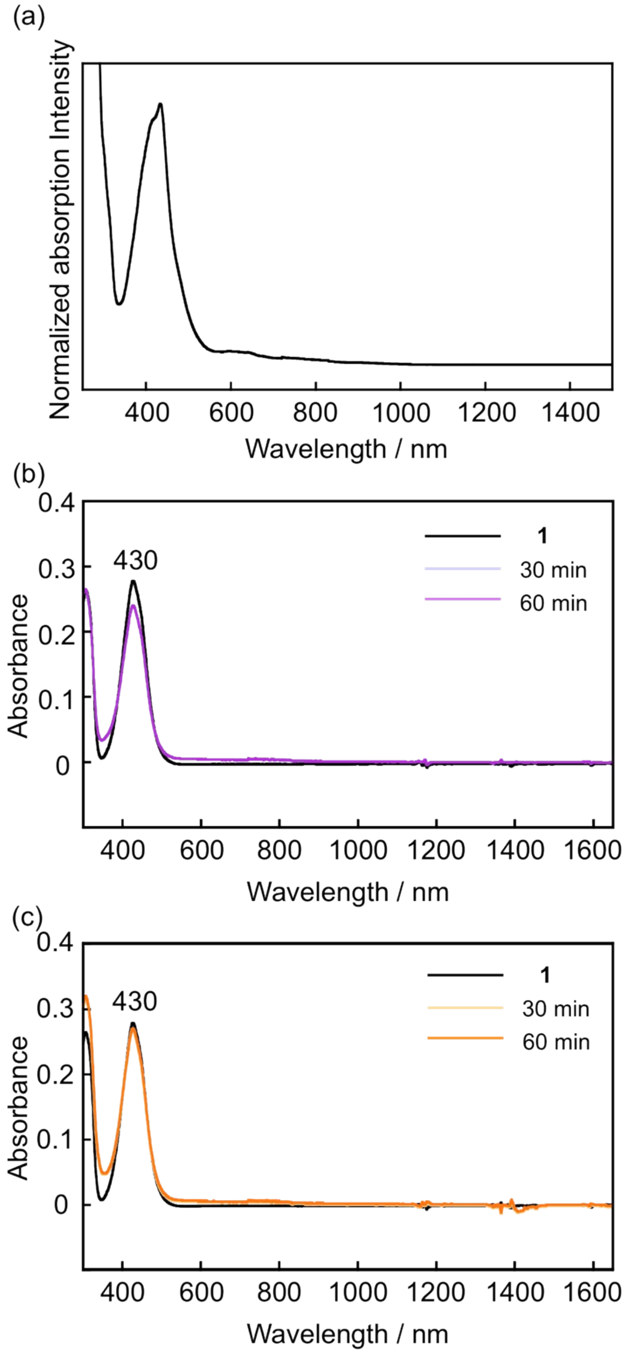


Figure S4. (a) UV-vis-NIR spectrum of electrocrystallized solution including **1** and $NaBPh_4$ in a CH_3CN solution. Time dependence of UV-vis-NIR spectra of **1** with (a) NaI and (b) $NaPF_6$ in a CH_3CN solution, respectively.

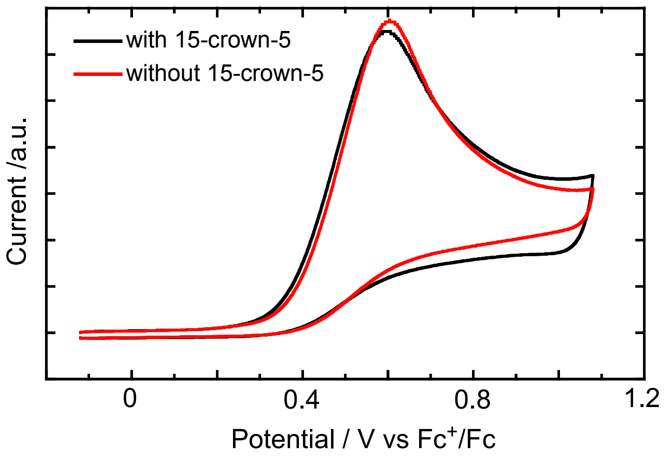


Figure S5. Cyclic voltammograms of $NaBPh_4$ in the presence/absence of 15-crown-5 (10 eq. relative to **1**) in CH_3CN solutions.

References

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