

Supporting Information

The Pyrazinacenes

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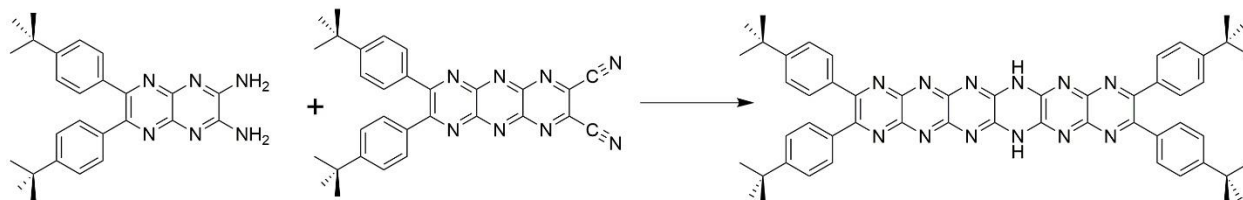
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General Experimental. Reagents and dehydrated solvents (in septum-sealed bottles) used for syntheses and spectroscopic measurements were obtained from Tokyo Kasei Chemical Co., Wako Chemical Co., Nacalai Tesque Chemical Co. or Aldrich Chemical Co. and were used without further purification. Electronic absorption spectra were measured using JASCO V-570 UV/Vis/NIR spectrophotometer. ATR-FTIR spectra were obtained using a Thermo-Nicolet 760X FTIR spectrophotometer equipped with a SMART-iTX ATR accessory. ¹H-NMR spectra were obtained using a JEOL JNM ECS400 spectrometer operating at 400 MHz using tetramethylsilane as a chemical shift reference. Proton decoupled ¹³C-NMR spectra were obtained using the same spectrometer operating at 101 MHz using tetramethylsilane as a chemical shift reference. ¹H NMR chemical shifts (δ) are reported in ppm relative to TMS in CDCl₃ (δ 0.00) or the residual solvent peak for other solvents. ¹³C NMR chemical shifts (δ) are reported in ppm relative to the solvent reported. MALDI-TOF mass spectra were measured using a Bruker Daltonics autoflex max mass spectrometer with dithranol as matrix. 6,7-Bis(4-*t*-butylphenyl)pyrazino[2,3-*b*]pyrazine-2,3-diamine¹ and 7,8-bis(4-*t*-butylphenyl)dipyrazino[2,3-*b*:2',3'-*e*]pyrazine-2,3-dicarbonitrile² were prepared according to previously reported methods.

2,3,10,11-Tetrakis(4-*t*-butylphenyl)-6,15-dihydro-1,4,5,6,7,8,9,12,13,14,15,16-dodecaazahexacene, (8).



Scheme S1. Synthesis of compound **8**.

N,N-Dimethylformamide (5 mL), 6,7-Bis(4-*t*-butylphenyl)pyrazino[2,3-*b*]pyrazine-2,3-diamine^{S1} (68 mg, 0.16 mmol), 7,8-bis(4-*t*-butylphenyl)dipyrazino[2,3-*b*:2',3'-*e*]pyrazine-2,3-dicarbonitrile^{S2} (50 mg, 0.10 mmol) and potassium carbonate (400 mg, 2.90 mmol) were placed in a round-bottomed flask, the resulting mixture was degassed followed by heating at 120 °C under a dry nitrogen atmosphere for 1 hour. The solvent was removed under reduced pressure and the residue dispersed in chloroform (150 ml), washed with water (100 ml), saturated aqueous ammonium chloride solution (2 × 150 ml) and the organic phase dried by standing over anhydrous magnesium sulfate. After filtration and removal of solvent under reduced pressure, the resulting solid was purified by column chromatography (SiO₂, CHCl₃/3% MeOH), gel permeation chromatography (Biobeads SX3, CHCl₃) then finally by column chromatography (SiO₂, CHCl₃/3% MeOH) to give the product as a dark blue solid. Yield: 12 mg (14 %). UV-vis (CH₂Cl₂): λ_{max} = 579, 541, 506, 468 nm. ¹H NMR (400 MHz, TFA-*d*, 20 °C): δ = 7.76 (dd, *J* = 8.5, 8.5 Hz, 16H, *ArH*), 1.53 (s, 36H, *CH*₃) ppm. ¹³C NMR (100 MHz, TFA-*d*, 20 °C): δ = 162.18, 159.32, 150.35, 147.63, 142.48, 132.40, 130.73, 128.82, 37.15, 31.71 ppm. FTIR (ATR): ν = 2960 (m, C-H(str)); 2905 (w, C-H(str)); 2867 (w, C-H(str)); 1608 (m), 1554 (m), 1520 (m), 1498 (w), 1475 (m) (C=C(str) and C=N(str)); 1420 (s), 1376 (s) (C-H(def)); 1268 (m), 1188 (s, C-N(str)); 1113 (s); 1075 (m); 1015 (m); 979 (w); 837 (w); 753 (w); 721 (w); 640 (w); 624 (w) cm⁻¹. MALDI-TOF-MS (dithranol): calc'd (C₅₄H₅₇N₁₂) 873.48, found 873.58 ([*M* + 3*H*]⁺)

Chemical Analytical Data for **8**.

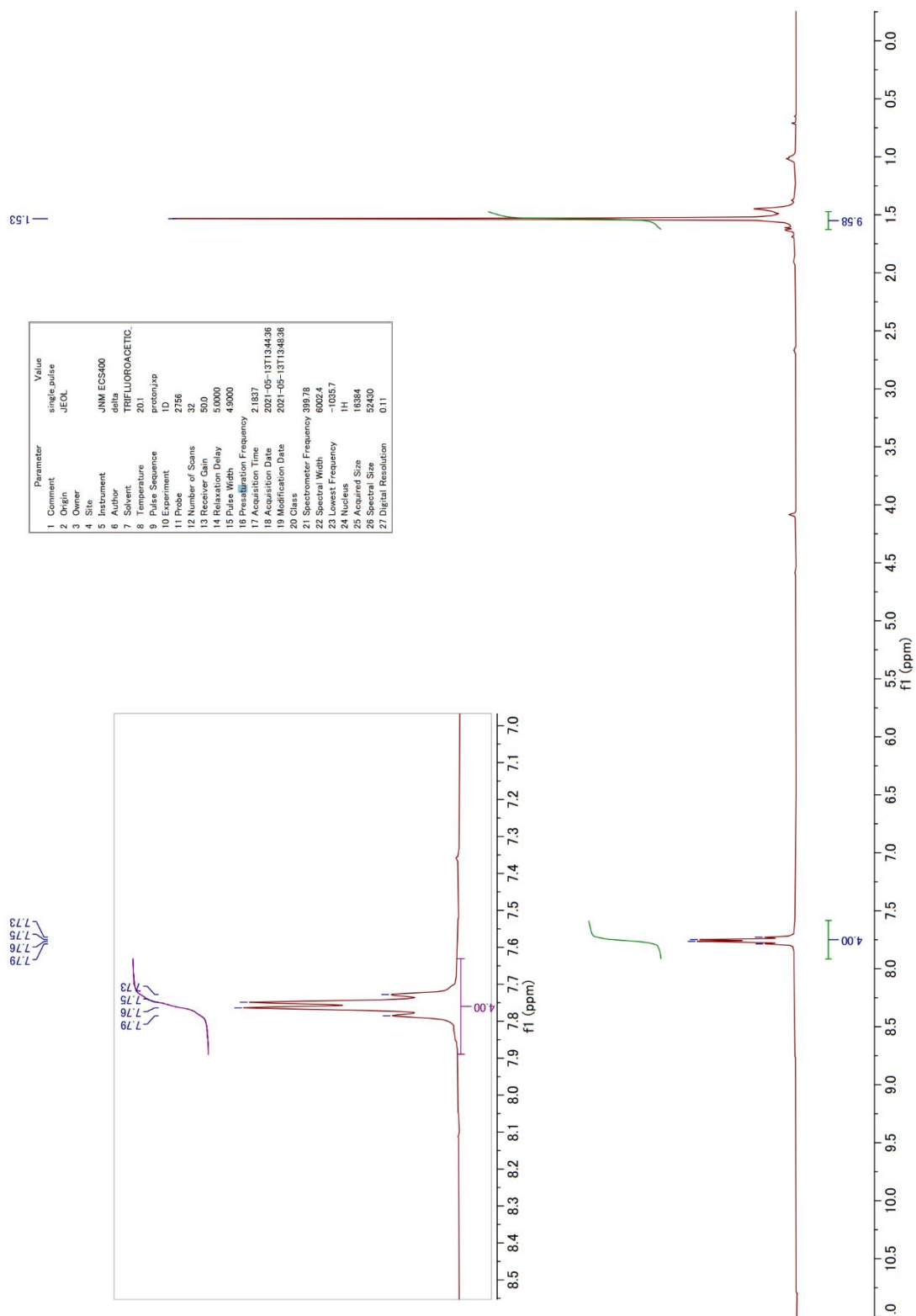


Figure S1. ^1H NMR Spectrum of compound **8** in trifluoroacetic acid-*d*.

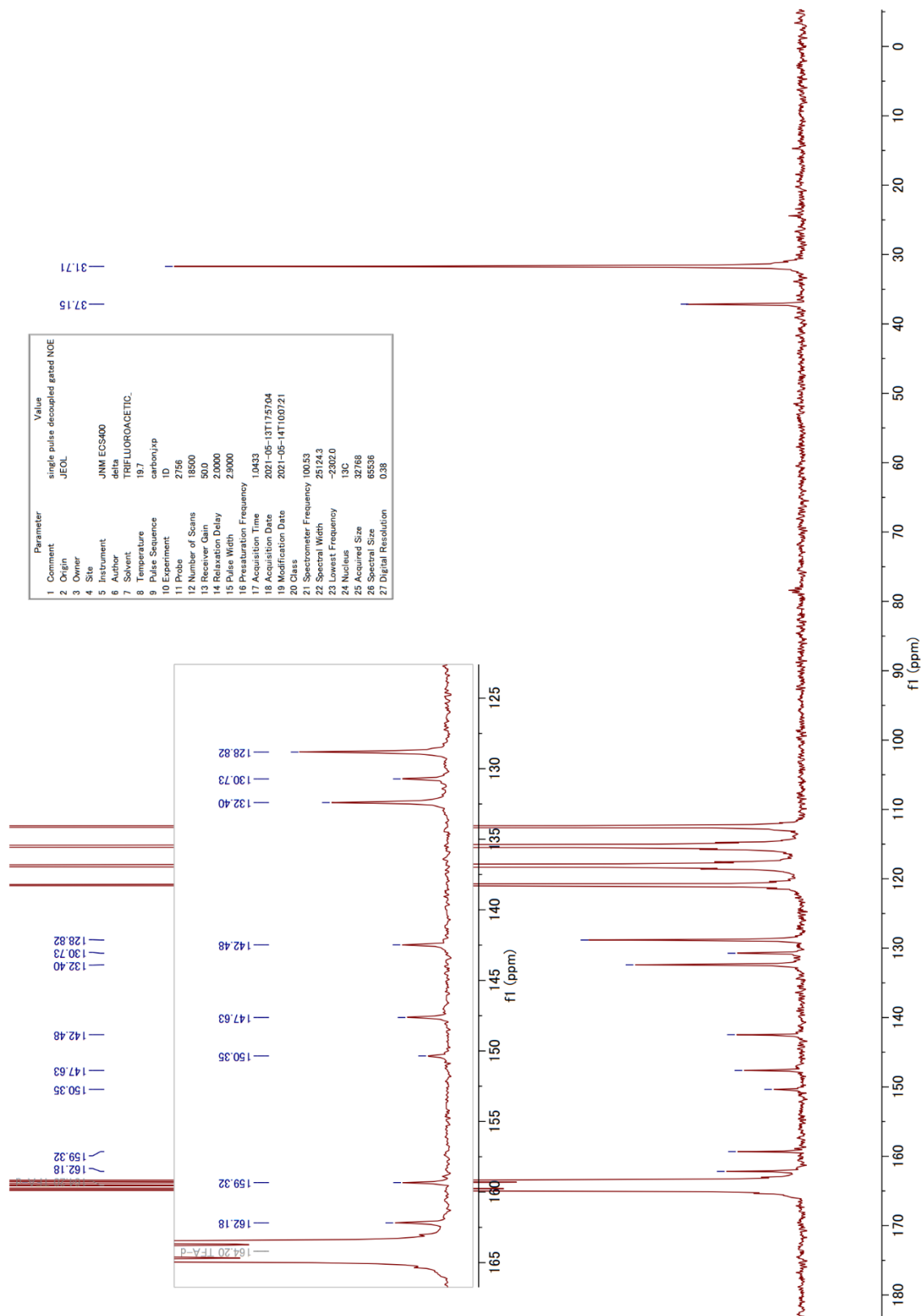


Figure S2. ¹³C NMR Spectrum of compound **8** in trifluoroacetic acid-d₄.

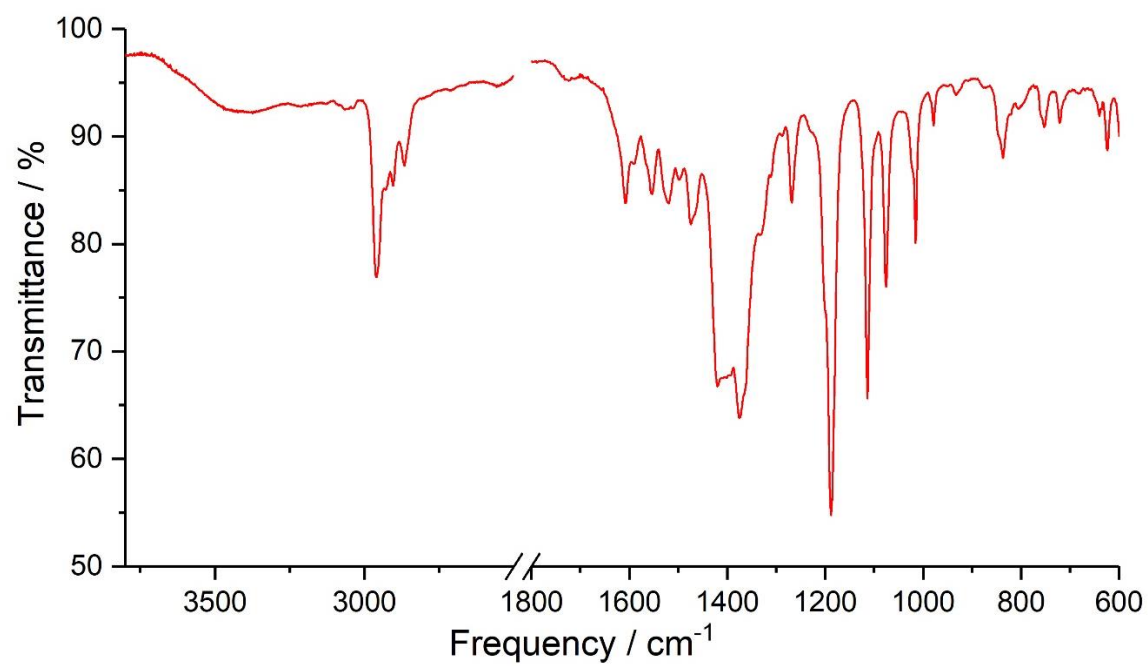


Figure S3. Infrared spectrum (ATR) of **8**.

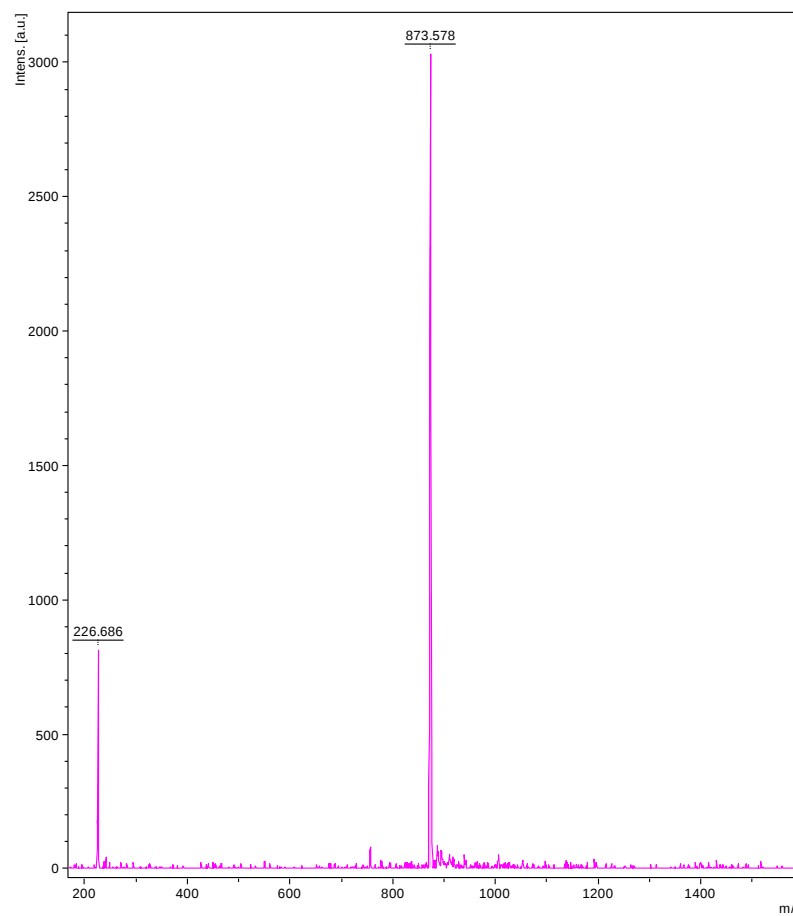


Figure S4. MALDI-TOF-MS spectrum of **8**. Dithranol was used as the matrix.

References

1. Miklík, D.; Mousavi, S. F.; Burešova, Z.; Middleton, A.; Matsushita, Y.; Labuta, J.; Ahsan, A.; Buimagalarinca, L.; Karr, P. A.; Švec, P.; Bureš, F.; Richards, G. J.; Mori, T.; Ariga, K.; Wakayama, Y.; Morari, C.; D'Souza, F.; Jung, T. A.; Hill, J. P. Pyrazinacenes exhibit On-Surface Oxidation-State-Dependent Conformational and Self-Assembly Behaviours. *Commun. Chem.* **2021**, *4*, 29. DOI: 10.1038/s42004-021-00470-w
2. Richards, G. J.; Hill, J. P.; Subbaiyan, N. K.; D'Souza, F.; Karr, P. A.; Elsegood, M. R. J.; Teat, S. J.; Mori, T.; Ariga, K. Pyrazinacenes: Aza Analogues of Acenes. *J. Org. Chem.* **2009**, *74*, 8914–8923. DOI: 10.1021/jo901832n