Electronic Supplementary Information

Dipyrrolylpyrazoles: anion receptors in protonated form and efficient building blocks for organized structures

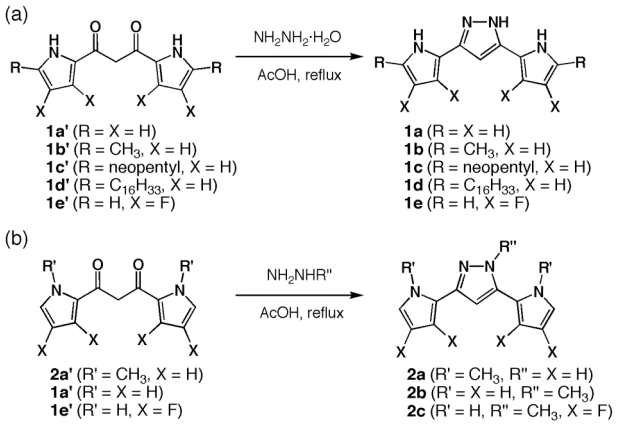
Hiromitsu Maeda,*[ab] Yoshihiro Ito,[a] Yukio Kusunose,[a] and Takashi Nakanishi[c]

Department of Bioscience and Biotechnology, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu 525-8577, Japan, Department of Applied Molecular Science, Institute for Molecular Science (IMS), Okazaki 444-8787, Japan, and National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan. Fax: +81 77 561 2659; Tel: +81 77 561 5969; E-mail: maedahir@se.ritsumei.ac.jp

Table of Contents

1. Synthetic procedures and spectroscopic data for 1a–e and 2a–c

Starting materials were purchased from Wako Chemical Co., Nacalai Chemical Co., and Aldrich Chemical Co. and used without further purification unless otherwise stated. UV-visible spectra were recorded on a Hitachi U-3500 spectrometer. Fluorescence spectra were recorded on a HITACHI F-4500 Fluorescence Spectrophotometer. NMR spectra used in the characterization of products were recorded on a JEOL AL-400 400 MHz and JEOL ECA-600HR 600 MHz spectrometers. All NMR spectra were referenced to solvent. Fast atom bombardment mass spectrometries (FAB-MS) were recorded on a JEOL-HX110 in the positive ion mode with a 3-nitrobenzylalcohol matrix. IR spectroscopies were recorded on a SHIMADZU FTIR-8600 spectrophotometer. TLC analyses were carried out on aluminum sheets coated with silica gel 60 (Merck 5554). Column chromatography was performed on Wakogel C-200, C-300, and Merck silica gel 60 and 60H. Synthesis of diketones **1a'**–**e'** and **2a'** were reported in the literature.[S1] 2-Alkylpyrroles as starting materials for the diketones were prepared according to literature procedures.[S2,S3]



Supporting Figure 1 Synthesis of (a) dipyrrolylpyrazole (dpp, **1a**–**e**) and (b) "protected" derivatives (**2a**–**c**) from dipyrrolyl-1,3-propanediones (**1a'**–**e'**, **2a'**).

3,5-Dipyrrol-2'-ylpyrazole, 1a. To a 40 ml of AcOH solution of 1,3-dipyrrolyl-1,3-propanedione (**1a'**) (198 mg, 0.98 mmol), 420 ml (6.86 mmol) of 80% solution of hydrazine monohydrate was added and stirred at reflux temperature for 87 h. After the monitoring of the consumption of the starting diketone on TLC, the solvent was removed and then the reaction mixture was separated by silica gel column chromatography (Wakogel C-200, CH_2Cl_2 to 0.5%TFA/CH_2Cl_2), followed by evaporation and recrystallization from hexane/CH_2Cl_2 to give TFA salts of dipyrrolylpyrazole **1a** as a colorless solid (63%). R_f = 0.50 (5%MeOH/CH_2Cl_2). ^{1}H NMR (DMSO-d_6, 400 MHz, 27 °C): δ (ppm) 12.64 (br, 1H, NH), 11.22 (br, 1H, NH), 11.10 (br, 1H, NH), 6.83 (s, 1H, αH), 6.70 (s, 1H, αH), 6.53 (s, 1H, pyrazole-CH), 6.46 (s, 1H, βH), 6.27 (s, 1H, βH), 6.09 (s, 1H, βH), 6.05 (s, 1H, βH). UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^4 $M^{-1}cm^{-1}$)): 270.5 (3.1). FABMS: *m/z* (% intensity): 198.2 (100, M^+). Calcd for $C_{11}H_{10}N_4$, 198.09.

3,5-Di-5'-methylpyrrol-2'-ylpyrazole, 1b. To a 40 ml of AcOH solution of dipyrrolyldiketone (**1b'**) (92 mg, 0.40 mmol), 1 ml (16 mmol) of 80% solution of hydrazine monohydrate was added and stirred at reflux temperature for 40 h. After the monitoring of the consumption of the starting diketone on TLC, the solvent was removed and then the reaction mixture was separated by silica gel column chromatography (Wakogel C-300, 2%MeOH/CH_2Cl_2), followed by evaporation and recrystallization from hexane/CH_2Cl_2 to give dipyrrolylpyrazole **1b** as a colorless solid (25%). R_f = 0.70 (5%MeOH/CH_2Cl_2). ^{1}H NMR (DMSO-d_6, 400 MHz, 27 °C): δ (ppm) 12.42 (br, 1H, NH), 10.83 (br, 2H, NH), 6.40 (s, 1H, pyrazole-CH), 6.26 (br, 1H, βH), 6.13 (br, 1H, βH), 5.73 (s, 2H, βH), 2.20 (s, 6H, CH_3). UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^4 $M^{-1}cm^{-1}$)): 281.5 (3.4). FABMS: *m/z* (% intensity): 226.2 (100, M^+), 227.2 (80, M^++1). Calcd for $C_{13}H_{14}N_4$, 226.12.

3,5-Di-5'-neopentylpyrrol-2'-ylpyrazole, 1c. To a 5 ml of AcOH solution of dipyrrolyldiketone (**1c'**) (14 mg, 0.04 mmol), 77 μl (1.2 mmol) of 80% solution of hydrazine monohydrate was added and stirred at reflux temperature for 48 h. After the monitoring of the consumption of the starting diketone on TLC, the solvent was removed and then the reaction mixture was separated by silica gel column chromatography (Wakogel C-300 3%MeOH/CH_2Cl_2), followed by evaporation and recrystallization from hexane/CH_2Cl_2 to give dipyrrolylpyrazole **1c** as a colorless solid (81%). R_f = 0.40 (5%MeOH/CH_2Cl_2). ^{1}H NMR (DMSO-d_6, 400 MHz, 27 °C): δ (ppm) 12.41 (br, 1H, NH), 10.73 (br, 2H, NH), 6.47 (s, 1H, pyrazole-CH), 6.35 (br, 1H, βH), 6.17 (br, 1H, βH), 5.74 (s, 2H, βH), 0.88 (s, 18H, CH_3). UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^4 $M^{-1}cm^{-1}$)): 283.5 (2.8). FABMS: *m/z* (% intensity): 338.2 (100, M^+), 339.2 (95, M^++1). Calcd for $C_{21}H_{30}N_4$, 338.25.

3,5-Bis(5'-hexadecylpyrrol-2'-yl)pyrazole, 1d. To a 20 ml of AcOH solution of dipyrrolyldiketone (**1d'**) (98 mg, 0.15 mmol), 370 ml (6.0 mmol) of 80% solution of hydrazine monohydrate was added and stirred at reflux temperature for 48 h. After the monitoring of the consumption of the starting diketone on TLC, the solvent was removed and then the reaction mixture was separated by silica gel column chromatography (Wakogel C-300, 3%MeOH/CH_2Cl_2), followed by evaporation and recrystallization from hexane/CH_2Cl_2 to give dipyrrolylpyrazole **1d** as a colorless solid (29%). R_f = 0.65 (5%MeOH/CH_2Cl_2). ^{1}H NMR (DMSO-d_6, 400 MHz, 27 °C): δ (ppm) 12.40 (br, 1H, NH), 10.81 (br, 1H, NH), 10.73 (br, 1H, NH), 6.44 (s, 1H, pyrazole-CH), 6.30 (br, 1H, βH), 6.10 (br, 1H, βH), 5.76 (s, 1H, βH), 5.71 (s, 1H, βH), 1.56 (s, 4H, CH_2), 1.22 (s, 52H, CH_2), 0.84 (t, J = 6.8 Hz, 6H, CH_3); ($CDCl_3$, 400 MHz, 27 °C; pyrazole NH cannot observed at the temperature.): δ (ppm) 9.42 (br, 2H, NH), 6.50 (s, 2H, βH), 6.40 (s, 1H, pyrazole-CH), 5.96 (s, 2H, βH), 2.63 (t, J = 7.6 Hz, 4H, pyrrole-CH_2), 1.67 (m, 4H, CH_2), 1.22 (m, 52H, CH_2), 0.85 (t, J = 6.8 Hz, 6H, CH_3). UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^4 $M^{-1}cm^{-1}$)): 283.0 (4.0). FABMS: *m/z* (% intensity): 646.3 (95, M^+), 647.3 (100, M^++1). Calcd for $C_{43}H_{74}N_4$, 646.59.

3,5-Bis(3',4'-difluoropyrrol-2'-yl)pyrazole, 1e. To a 15 ml of AcOH solution of dipyrrolyldiketone (**1e'**) (93 mg, 0.34 mmol), 750 ml (12.3 mmol) of 80% solution of hydrazine monohydrate was added and stirred at reflux temperature for 33 h. After the monitoring of the consumption of the starting diketone on TLC, the solvent was removed and then the reaction mixture was separated by flash silica gel column chromatography (eluent: 2%MeOH/CH_2Cl_2), followed by evaporation and recrystallization from hexane/CH_2Cl_2 to give dipyrrolylpyrazole **1e** as a colorless solid (54%). R_f = 0.30 (5%MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 600 MHz, 27 °C): δ (ppm) 7.85 (br, 1H, NH), 6.53 (s, 1H, pyrazole-CH), 6.50 (m, 1H, αH). (DMSO-d_6, 600 MHz, 27 °C): δ (ppm) 12.93 (s, 1H, NH), 11.08 (s, 1H, NH), 6.87 (s, 1H, αH), 6.64 (s, 1H, αH), 6.56 (s, 1H, pyrazole-CH). UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^4 $M^{-1}cm^{-1}$)): 266.5 (3.0). ESIMS: *m/z* (% intensity): 270.1 (100, M^-–1). Calcd for $C_{11}H_6F_4N_4$, 270.05.

3,5-Di-1'-methylpyrrol-2'-ylpyrazole, 2a. To a 10 ml of AcOH

solution of N-methyl-substituted dipyrrolyldiketone (**2a'**) (100 mg, 0.42 mmol), 1.0 ml (16.3 mmol) of 80% solution of hydrazine monohydrate was added and stirred at reflux temperature for 72 h. After the monitoring of the consumption of the starting diketone on TLC, the solvent was removed and then the reaction mixture was separated by silica gel column chromatography (Wakogel C-300, CH_2Cl_2 to 3%MeOH/CH_2Cl_2), followed by evaporation and recrystallization from hexane/CH_2Cl_2 to give dipyrrolylpyrazole **2a** as a colorless solid (6%). R_f = 0.60 (5%MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz, 27 °C; pyrazole NH cannot observed at the temperature.): δ (ppm) 6.72 (m, 2H, αH), 6.44 (m, 3H, βH and pyrazole-CH), 6.19 (m, 2H, βH), 3.83 (s, 6H, CH_3). UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^4 $M^{-1}cm^{-1}$)): 270.0 (2.5). FABMS: *m/z* (% intensity): 226.3 (100, M^+). Calcd for $C_{13}H_{14}N_4$, 226.12.

1-Methyl-3,5-dipyrrol-2'-ylpyrazole, 2b. *Route a*: To a 10 ml of 2-propanol solution of dipyrrolylpyrazole (**1a**) (30 mg, 0.15 mmol), 10 ml of 29% NaOH aq and 77 μl (1.24 mmol) of CH_3I were added and stirred at 35 °C for 8 h. After the monitoring of the consumption of the starting material on TLC, the mixture was extracted into ether, washed saturated NaCl aq, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was separated by silica gel column chromatography (Wakogel C-300, 2%MeOH/CH_2Cl_2), followed by evaporation and recrystallization from hexane/CH_2Cl_2 to give dipyrrolylpyrazole **2b** as a colorless solid (93%). *Route b*: To a 10 ml of AcOH solution of 1,3-dipyrrolyl-1,3-propanedione (**1a'**) (40 mg, 0.20 mmol), 250 ml (4.7 mmol) of methylhydrazine was added and stirred at reflux temperature for 4 h. After the monitoring of the consumption of the starting diketonson TLC, the solvent was removed and then the reaction mixture was separated by silica gel column chromatography (Wakogel C-300, 3%MeOH/CH_2Cl_2), followed by evaporation and recrystallization from hexane/CH_2Cl_2 to give dipyrrolylpyrazole **2b** as a colorless solid (5%). R_f = 0.50 (5%MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz, 27 °C): δ (ppm) 9.05 (br, 1H, NH), 8.40 (br, 1H, NH), 6.93 (s, 1H, αH), 6.81 (s, 1H, αH), 6.42–6.35 (m, 4H, βH and pyrazole-CH), 6.24 (s, 1H, βH), 3.96 (s, 3H, CH_3). UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^4 $M^{-1}cm^{-1}$)): 270.5 (2.1). FABMS: *m/z* (% intensity): 212.3 (100, M^+). Calcd for $C_{12}H_{12}N_4$, 212.11.

1-Methyl-3,5-bis(3',4'-difluoropyrrol-2'-yl)pyrazole, 2c. To a 6 ml of 2-propanol solution of dipyrrolylpyrazole (**1e**) (20 mg, 7.4×10^{-2} mmol), 6 ml of 23% NaOH aq and 28 μl (0.45 mmol) of CH_3I were added and stirred at 35 °C for 5.5 h. After the monitoring of the consumption of the starting material on TLC, the mixture was extracted into ether, washed saturated NaCl aq, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was separated by silica gel column chromatography (Wakogel C-300, 1%MeOH/CH_2Cl_2), followed by evaporation and recrystallization from hexane/CH_2Cl_2 to give dipyrrolylpyrazole **2c** as a colorless solid (28%). R_f = 0.51 (5% MeOH/CH_2Cl_2). ^{1}HNMR ($CDCl_3$, 600 MHz, 27°C): δ (ppm) 8.00 (br, 1H, NH), 7.41 (br, 1H, NH), 6.59 (s, 1H, αH), 6.48 (s, 1H, pyrazole-CH), 6.42 (s, 1H, αH). (DMSO-d_6, 400 MHz, 27°C): δ (ppm) 11.20 (br, 1H, NH), 11.08 (br, 1H, NH), 6.93 (s, 1H, αH), 6.65 (s, 1H, αH), 6.49 (s, 1H, pyrazole-CH). UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^4 $M^{-1}cm^{-1}$)): 261.5 (2.4). FABMS: *m/z* (% intensity): 283.9 (100, M^+). Calcd for $C_{12}H_8F_4N_4$, 284.07.

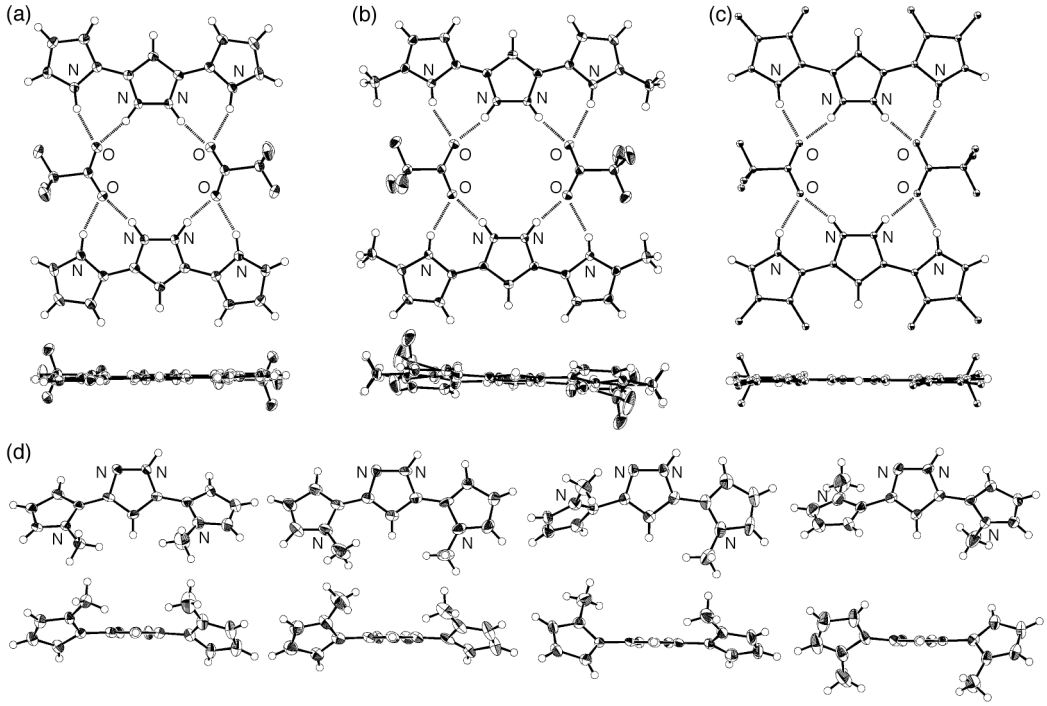
[S1] (a) Oddo, B.; Dainotti, C. *Gazz. Chim. Ital.* **1912**, *42*, 716. (b) Stark, W. M.; Baker, M. G.; Leeper, F. J.; Raithby, P. R.; Battersby, A. R. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1187. (c) Maeda, H.; Kusunose, Y. *Chem. Eur. J.* **2005**, *11*, 5661. (d) Fujimoto, C.; Kusunose, Y.; Maeda, H. *J. Org. Chem.* **2006**, *71*, 2389. (d) Maeda, H.; Ito, Y. *Inorg. Chem.* **2006**, *45*, 8205. (e) Maeda, H.; Kusunose, Y.; Terasaki, M.; Ito, Y.; Fujimoto, C.; Fujii, R.; Nakanishi, T. to be submitted.

[S2] Yadav, J. S.; Reddy, B. V. S.; Kondaji, G.; Rao, R. S.; Kumar, S. P. *Tetrahedron Lett.* **2002**, *43*, 8133.

[S3] Greenhouse, R.; Ramirez, C. *J. Org. Chem.* **1985**, *50*, 2961.

2. Single-crystal diffraction analysis

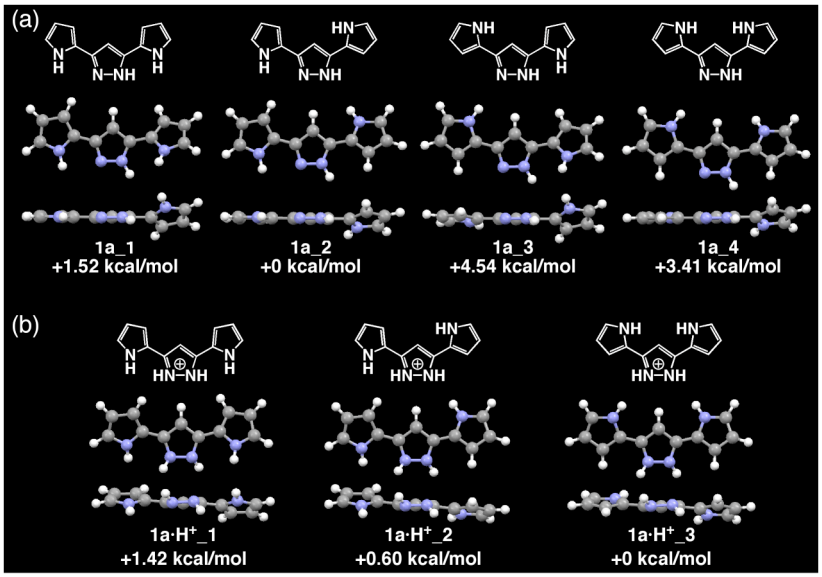
Method for X-ray analysis: A single crystal of **1a**·TFA was obtained by vapor diffusion of hexane into a CH_2Cl_2 solution of **1a** with equivalent of TFA. The data crystal was a colorless prism of approximate dimensions 0.50 × 0.20 × 0.20 mm. Data were collected at 120 K on a Bruker SMART CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), and structure was solved by direct method. A single crystal of **1a**·TFA was obtained by vapor diffusion of hexane into a CH_2Cl_2 solution of **1b** with equivalent of TFA. The data crystal was a colorless prism of approximate dimensions 0.50 × 0.30 × 0.10 mm. Data were collected at 123 K on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71075 Å), and structure was solved by direct method. A single crystal of **1e**·TFA was obtained by vapor diffusion of hexane into a CH_2Cl_2 solution of **1e** with equivalent of TFA. The data crystal was a colorless prism of approximate dimensions 0.55 × 0.30 × 0.30 mm. Data were collected at 123 K on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71075 Å), and structure was solved by direct method. A single crystal of **2a** was obtained by vapor diffusion of hexane into a CH_2Cl_2 solution of **2a**. The data crystal was a colorless prism of approximate dimensions 0.10 × 0.10 × 0.05 mm. Data were collected at 123 K on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71075 Å), and structure was solved by direct method. In each case, the non-hydrogen atoms were refined anisotropically. The calculations were performed using the Crystal Structure crystallographic software package of Molecular Structure Corporation. CIF files (CCDC-625142–625145 for **1a**·TFA, **1b**·TFA, **1e**·TFA, and **2a**) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



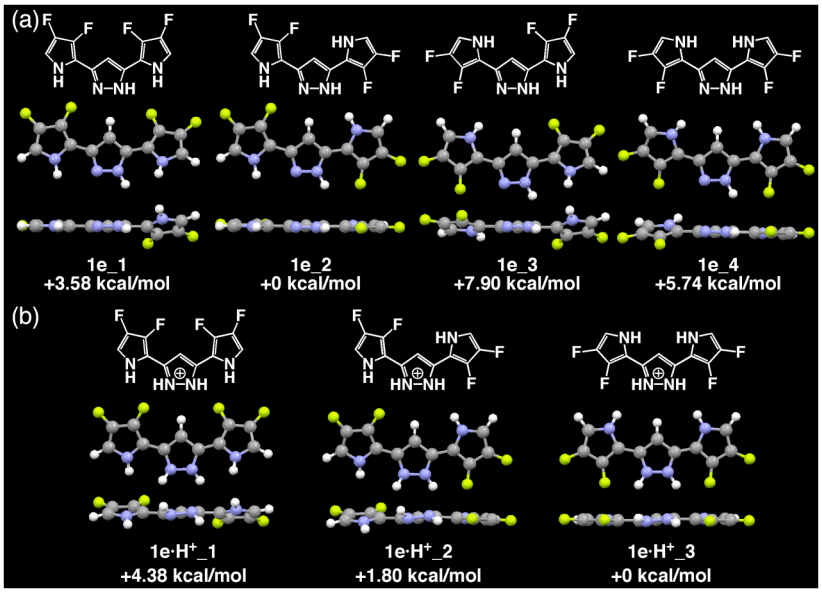
Supporting Figure 2 Ortep drawings (top and side view) of X-ray single crystal structures of (a) **1a**·TFA, (b) **1b**·TFA, (c) **1e**·TFA, and (d) **2a** (four conformations). Thermal ellipsoids are scaled to the 50% probability level.

3. Optimization of dipyrrolylpyrazoles 1a,e and protonated forms by DFT calculations at the level of B3LYP/6-31G**

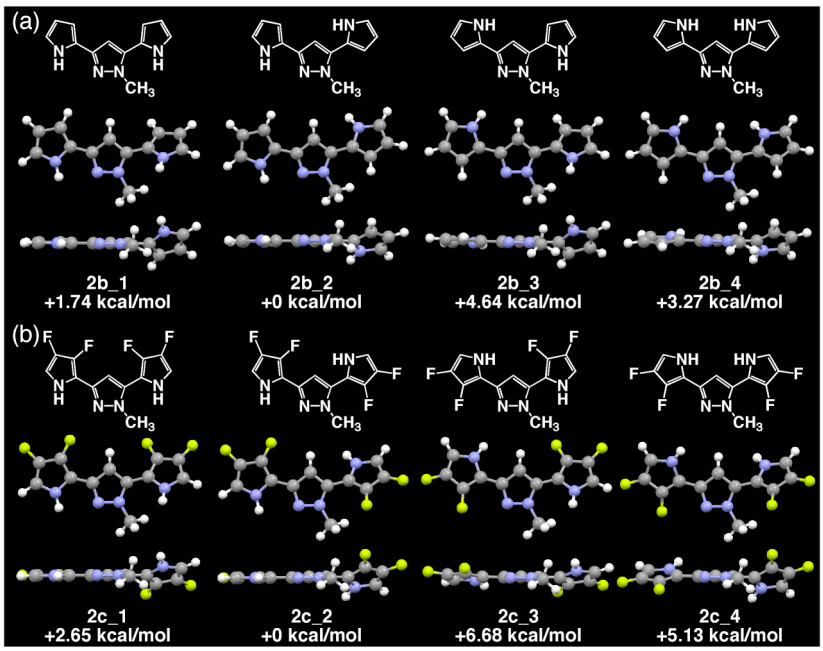
Method for DFT calculations: Ab initio calculations of neutral and protonated forms of **1a** and its anion binding complexes were carried out using Gaussian 03 program[4] and an HPC-alpha UP264 (HIT) computer. The structures were optimized, and the total electronic energies were calculated at the B3LYP level using a 6-31G** basis set.



Supporting Figure 3 Optimized structures and relative energies compared to the most stable isomers of (a) neutral *dpp* **1a** and (b) protonated **1a** by DFT calculations (B3LYP/6-31G(d,p) level).



Supporting Figure 4 Optimized structures and relative energies compared to the most stable isomers of (a) neutral *dpp* **1e** and (b) protonated **1e** by DFT calculations (B3LYP/6-31G(d,p) level).



Supporting Figure 5 Optimized structures and relative energies compared to the most stable isomers of (a) **2b** and (b) **2c** by DFT calculations (B3LYP/6-31G(d,p) level).

Cartesian Coordination of 1a_1.
–644.1858658 hartree
C,-2.5252682308,0.2569441539,0.0806636935
C,0.0266109499,0.6860151325,-0.0106578652
C,2.5310855993,0.0371221161,-0.1245448295
C,1.0984545958,-0.1883934666,-0.0819472201
C,-4.747463646,-0.0940740547,0.1757025164
C,-1.1300679982,-0.1365743811,0.0014486541
C,-4.5465650115,1.2723169306,0.1979847597
C,3.2763625537,1.0381567177,-0.7251266275
C,4.7118198604,-0.3809002837,0.285932505
C,-3.1451713556,1.4963326256,0.1384511069
C,4.6478325563,0.7725851902,-0.4659421994
N,-0.8047732369,-1.4356948677,-0.0569666401
N,0.5497333865,-1.4431443161,-0.0876606257
N,-3.5188686688,-0.6960887333,0.1050074556
N,3.4272957046,-0.8322004676,0.474961338
H,0.0785761042,1.7610310513,0.0640253558
H,-5.6562323487,-0.6763421308,0.2045190754
H,-5.320458998,2.0248149241,0.2516160421
H,2.8689954669,1.8465884951,-1.3149421675
H,5.5559131481,-0.9138407118,0.6970633901
H,-2.6420355432,2.4529775934,0.1360771153
H,5.4936430686,1.3541107102,-0.8039078263
H,1.0237245556,-2.306670911,-0.3004259801
H,-3.3249566642,-1.6849182813,0.0722749421
H,3.1633416737,-1.5650361287,1.1145223954

Cartesian Coordination of 1a_2.
–644.1882821 hartree
C,-2.5193634227,0.0711044439,0.0278955308
C,0.0134752756,0.6090362185,0.0326662485
C,2.547620187,0.0522172934,0.018068932
C,1.1252302412,-0.2228747375,0.0103085674
C,-4.7261417914,-0.3766696894,0.0434002949
C,-1.1063182039,-0.2615550579,0.0082584584
C,-4.5863757691,0.9973501847,0.0566068328
C,4.8059921703,0.0541774315,0.2237203666
C,-3.194743255,1.282346085,0.047142196
C,4.4233726392,1.2482173594,-0.3512463534
C,3.6269386708,-0.7014549783,0.4583051941
N,3.0560861855,1.2399348184,-0.4659175434
N,-0.7217622343,-1.5456222699,-0.0273797344
N,0.6294414899,-1.4931034108,-0.0225087045
N,-3.4704081259,-0.9244311698,0.0261327976
H,0.0075053,1.6859073836,0.1086336071
H,-5.6088649015,-0.9984164927,0.0454064983
H,-5.394021359,1.7153023862,0.0719893314
H,5.8189108829,-0.238071114,0.4606448897
H,-2.7345117136,2.2604288476,0.0528971361
H,5.0064448005,2.0937260449,-0.6836828807
H,3.5651225569,-1.6698318441,0.9353175749
H,2.5015129996,1.9516778629,-0.9140524102
H,1.1584274734,-2.3454860753,-0.1142205235
H,-3.2321476981,-1.9040500944,0.0140214609

Cartesian Coordination of 1a_3.
–644.1810453 hartree
C,-0.5785409084,-0.0306316756,-2.4410404299
C,-0.5534164626,0.0145504122,0.148290088
C,0.5072207931,-0.0064241494,2.5090428813
C,0.5386970612,-0.0608757041,1.0568355684
C,-0.7133661363,0.4554584379,-4.6421527832
C,0.0099273894,-0.06155579,-1.1154168747
C,-1.8549957546,-0.2384995038,-4.3030550289
C,0.9430870638,0.1263627897,4.7292149463
C,-1.7727940217,-0.5451725939,-2.918222695
C,-0.4205406207,-0.0102025196,4.5665210109
C,1.5285288272,0.1282539485,3.436172726
H,-1.6004412421,0.1689878957,0.3625647776

H,-0.3919700004,0.8758959058,-5.5831400224
H,-2.6543564296,-0.5082547006,-4.97831083
H,1.4602038336,0.2184883862,5.6738494517
H,-2.4829212623,-1.1117632843,-2.3332024267
H,-1.221160469,-0.0589429331,5.2892205787
H,2.5750452044,0.2254188716,3.1882605
H,-1.581866906,-0.2336762041,2.8091273994
H,2.062212155,-0.3801858112,-1.589881233
H,0.8801564211,1.1497765224,-3.4315432655
N,-0.674768765,-0.0841134517,3.2193043635
N,1.358087996,-0.1558596849,-0.9044275579
N,1.702776603,-0.1772413319,0.404253944
N,0.0642263536,0.5638821029,-3.513999519

Cartesian Coordination of 1a_4.

–644.1828482 hartree

C,-2.5402932719,-0.1534454428,0.021861309
C,-0.0333101775,0.5025173709,0.0342290215
C,2.5273602467,0.0712964046,0.0210699081
C,1.119745972,-0.2718952506,0.0060196626
C,-4.805682725,-0.2295570866,0.0441080745
C,-1.1121837713,-0.4234953276,0.0004387925
C,-4.4204951714,1.0952812608,0.069539583
C,4.7812863511,0.1823494819,0.246549278
C,4.3492319469,1.3483165008,-0.3501844201
C,-3.6249602804,-1.0163891843,0.014704644
C,3.6363569757,-0.623870062,0.4828375618
N,2.9844597854,1.2749668458,-0.4757863255
N,-3.047702966,1.1307846141,0.0546739458
N,-0.6612422709,-1.6844837272,-0.0475092299
N,0.6835796514,-1.5619362985,-0.0417638496
H,-0.0755355339,1.5783968063,0.1258424049
H,-5.8242635553,-0.5912011165,0.0473016812
H,-5.0020455527,2.004594903,0.0965202596
H,5.8042287715,-0.0585566485,0.497479865
H,4.8957544538,2.2146097812,-0.6913343733
H,-3.5527857552,-2.0935497023,-0.0082887514
H,3.6145304407,-1.586123389,0.9751680497
H,2.4035421771,1.947960571,-0.9494300998
H,-2.4924983816,1.9699870166,0.0676056057
H,1.2530769678,-2.3880902522,-0.135206917

Cartesian Coordination of 1a·H^+_1.

–644.5720182 hartree

C,-2.4913559818,0.0594115132,-0.2967385456
C,-0.01477459,0.6146156827,-0.0284500535
C,2.4850030149,0.2055099724,0.284491599
C,1.1191157419,-0.176396469,0.1722847587
C,-4.6683395466,-0.2753678653,-0.7301502481
C,-1.1090909487,-0.2450048307,-0.1528965662
C,-4.5347264508,1.0353933473,-0.2929375096
C,3.1091987358,1.3975476584,-0.0966882271
C,4.6743460709,0.0158512889,0.7423438145
C,-3.1722862642,1.2507756562,-0.0260158649
C,4.4797255331,1.272669004,0.1861872054
N,-0.6442189268,-1.5450996221,-0.0941742987
N,0.7172404198,-1.4972101335,0.2351243509
N,-3.4415402408,-0.8670673749,-0.7103193149
N,3.4770817495,-0.6328431382,0.7795127462
H,-0.0406722779,1.6913420138,-0.0784443118
H,-5.5425629798,-0.816916813,-1.0604683272
H,-5.338717216,1.746879591,-0.1775089706
H,2.6191117329,2.239193956,-0.5650527024
H,5.5724734617,-0.4509205537,1.1194719957
H,-2.7235041119,2.1544312813,0.3613105382
H,5.249223038,2.0078948358,0.0036797231
H,-1.1703661012,-2.2377523964,0.4307338814
H,1.2770789461,-2.2090168499,-0.2252197204
H,-3.2404744748,-1.764042327,-1.1270485939
H,3.3175770834,-1.4955806054,1.2789599283

Cartesian Coordination of 1a·H^+_2.

–644.5733282 hartree

C,-2.4865693723,0.0927175252,0.2118351201
C,0.0204786735,0.5607829862,0.0580858583
C,2.5242857176,0.0304265731,-0.1894154908
C,1.1385196093,-0.2739147196,-0.0706918072
C,-4.7186582395,-0.1419158958,0.160991422
C,-1.1151746908,-0.2523744989,0.0438162135
C,-4.4493453268,1.0868686158,0.7467490913
C,4.7879931523,-0.00175305,-0.2564836358
C,-3.0523341723,1.2401661467,0.7748834538
C,4.3521951889,1.3014434217,-0.4639722723
C,3.6460215499,-0.8007536058,-0.0858719288
N,2.9945196747,1.31585595,-0.4128780185
N,-0.7038084604,-1.5547212903,-0.1558619225
N,0.6904297643,-1.5716988805,-0.0970371146
N,-3.5357853358,-0.7482754598,-0.1390708711
H,0.0212288934,1.6349685382,0.1535438406
H,-5.6614608672,-0.6162142809,-0.0686754763
H,-5.1857912312,1.7850400539,1.1155733422
H,5.8175170371,-0.3254614005,-0.2237100378
H,-2.5009359469,2.0688225469,1.1960783194
H,4.9137250265,2.2060806868,-0.6446462243
H,3.6304217091,-1.8595942805,0.1331389139
H,2.4236930607,2.1284330303,-0.5896334701
H,-1.1527788894,-2.3073534886,0.3577970047
H,1.1473062917,-2.2762393233,-0.6649823429
H,-3.454887122,-1.5767653093,-0.7101045271

Cartesian Coordination of 1a·H^+_3.

–644.5742799 hartree

C,-2.5148056251,-0.0491208808,0.1807048591
C,-0.0042870383,0.5123806926,0.0595097158
C,2.5149327591,0.0353003609,-0.1823892455
C,1.131654046,-0.2948019684,-0.08593304
C,-4.7791071683,-0.0846958481,0.2026792169
C,-1.1264470168,-0.3253025661,0.0137575194
C,-4.34623052,1.1298815666,0.7184628456
C,4.7794713033,0.0433435434,-0.2073550646
C,4.3254978605,1.3364918535,-0.4314988705
C,-3.6343825143,-0.8270377146,-0.1333627264
C,3.6478769518,-0.7752201389,-0.0530089401
N,2.9659947786,1.3276807214,-0.4032555976
N,-2.986807627,1.1503697042,0.6915409872
N,-0.6804148376,-1.6013183606,-0.2176965479
N,0.7072339703,-1.5970852687,-0.1543440836
H,-0.0132334963,1.5838163673,0.1841349919
H,-5.8080678761,-0.3868076439,0.0772348973
H,-4.9094668705,1.9682045051,1.1008982664

H,5.8135418845,-0.2623583814,-0.152498474
H,4.8739787345,2.2494937912,-0.610219928
H,-3.6157421559,-1.8032955301,-0.5980204211
H,3.6463014091,-1.8322552014,0.1751641592
H,2.3848945454,2.1251980175,-0.6116261145
H,-2.4185846984,1.8884968151,1.0780985824
H,-1.1457638994,-2.4099660485,0.1784837947
H,1.1850602059,-2.2853676644,-0.7247606786

Cartesian Coordination of 1e_1.

–1041.0718473 hartree

C,-0.1241806649,-2.5588261393,0.0888975683
C,-0.1419653993,0.019912849,0.0837489444
C,0.8917572786,2.3816228092,0.0909294558
C,0.8967129037,0.9366941345,0.0834182384
C,-0.1988192492,-4.8244327995,0.0904536326
C,0.4911500626,-1.2487478532,0.0786263086
C,-1.4975314444,-4.359761383,0.1026930953
C,-0.0527278674,3.269659063,-0.3905322611
C,1.6439152891,4.4968568307,0.4526201569
C,-1.4529523078,-2.9481879935,0.1023110578
C,0.4194234288,4.5843246931,-0.1672821903
F,-2.6103942008,-5.1068424076,0.114041541
F,-1.1965278425,2.9379839416,-0.9994173704
F,-2.5105150395,-2.1204792076,0.1134792393
F,-0.2144489206,5.7068441693,-0.5234397459
N,1.8262992546,-1.1378159342,0.0718523523
N,2.0497426398,0.1979110647,0.091525374
N,0.6165070943,-3.7197144054,0.0827502319
N,1.9369758149,3.1542828175,0.576086629
H,-1.1983789565,0.2325224725,0.1057255302
H,0.1819070422,-5.8325359865,0.0870423963
H,2.3086381501,5.2700865218,0.8012323697
H,2.985848468,0.5316955635,-0.0749705352
H,1.6240891801,-3.7154696968,0.0716955176
H,2.6295043403,2.7988126009,1.2164955968

Cartesian Coordination of 1e_2.

–1041.0775509 hartree

C,-0.5147970708,-2.5513363148,-0.0049404686
C,-0.5192743718,0.0235701844,-0.0065700323
C,0.5634425678,2.3799997554,0.006337054
C,0.5261883387,0.9373739904,0.006203327
C,-0.6142423134,-4.815790147,-0.0051284045
C,0.1097312178,-1.2458614158,0.0020059824
C,-1.9079299611,-4.3372513713,-0.0208782528
C,1.1739966514,4.5669318247,0.0117387661
C,-1.8473738895,-2.926449621,-0.0208560144
C,-0.2035380651,4.5159881811,-0.0027650156
C,1.6502735484,3.2396389648,0.0173671503
F,-3.0293613612,-5.0717120089,-0.0340323055
F,-2.895903415,-2.0836889023,-0.033923007
N,-0.5547981943,3.1864843048,-0.0058980741
N,1.4451005878,-1.1370352129,0.0182487729
N,1.6707445954,0.193942733,0.0202524507
N,0.2130352217,-3.7195239952,0.0044239885
F,1.9306386682,5.6701084623,0.0191903642
F,2.939557785,2.8460944821,0.0314449603
H,-1.5804526297,0.2168953728,-0.0200061966
H,-0.2440976727,-5.8277932639,-0.0002805131
H,-0.9314965262,5.3102914459,-0.0110362443
H,-1.500705712,2.8420352139,-0.0151103751
H,2.614172929,0.5494860476,0.0312345784
H,1.2207591301,-3.7260921088,0.0168041278

Cartesian Coordination of 1e_3.

–1041.0649595 hartree

C,-0.4534364325,-2.5595795291,-0.0306815069
C,-0.4373450798,0.0155542856,-0.0848338258
C,0.5874049561,2.3777524223,-0.0175359273
C,0.6453322104,0.9290355639,0.0337889327
C,-0.5927527258,-4.8061207331,-0.3522376383
C,0.1357799854,-1.2416048079,0.0213075729
C,-1.8172780869,-4.367395518,0.0951829075
C,0.9636487256,4.6069502312,-0.1867740078
C,-1.7343162253,-2.9697362088,0.2924018191
C,-0.3861562028,4.4326779918,0.0217532966
C,1.5735437471,3.3321605668,-0.2102229639
F,-2.8974931057,-5.1209658941,0.3277376976
F,1.5979549227,5.775494084,-0.3536309606
F,-2.7132971807,-2.1791249518,0.750459076
F,2.8735770746,3.0997458725,-0.4153775025
N,-0.5996267827,3.0767035155,0.1050172366
N,1.4762255119,-1.0213820407,0.1775872576
N,1.8091637478,0.2888124345,0.2044859189
N,0.2366546593,-3.70499079,-0.3970091801
H,-1.4799958623,0.219852121,-0.2740491347
H,-0.2622019652,-5.7930996415,-0.6311982264
H,-1.1808241136,5.154684039,0.1127151302
H,-1.4712521668,2.6533819508,0.3774772756
H,2.1822592933,-1.697631176,0.4225730171
H,1.1018702335,-3.6856967123,-0.9136734407

Cartesian Coordination of 1e_4.

–1041.0684054 hartree

C,-0.7825485753,-2.4205343887,0.0513792491
C,-0.8118383727,0.156035048,-0.0052963633
C,0.2294701014,2.5336250142,0.0302190582
C,0.2134242822,1.0909015688,0.0670948239
C,-1.313662129,-4.6156044857,-0.1464731494
C,-0.1658664584,-1.1069864807,0.0807330952
C,-2.4601312245,-3.9486043733,0.2201274969
C,0.8068642384,4.730228384,0.0400709987
C,-0.5593485017,4.6573844135,-0.1261925975
C,-0.2672172172,-3.6700442055,-0.2505084301
C,1.2967961181,3.4112733554,0.136699942
F,-1.1995926448,-5.9290330582,-0.3852035428
F,1.5438057543,5.844498641,0.1020017474
F,0.9877824512,-3.9437691028,-0.6178104002
F,2.5809114822,3.0420568694,0.3066575675
N,-0.8913627555,3.3223347144,-0.1267617199
N,-2.1273934359,-2.6158614494,0.313515425
N,1.1609228179,-0.9684918889,0.2004520617
N,1.3613058469,0.3638936348,0.1838774124
H,-1.8655830224,0.3516086265,-0.1418090994
H,-3.4548444142,-4.3159649709,0.4117648302
H,-1.2919140518,5.4392835513,-0.2397176517
H,-1.8229395766,2.9643100679,-0.2556182959
H,-2.7181136314,-1.9138859027,0.7276817477
H,2.2972704286,0.7317003074,0.2621831241

Cartesian Coordination of 1e·H$^+$_1.

–1041.4462554 hartree

C,-0.0489903392,0.0337014175,-2.533640387
C,-0.0469454494,-0.0000241073,0.009050102
C,0.8963016514,-0.033991286,2.370309913
C,0.9818288431,-0.0461596649,0.9536435189
C,-0.2751260056,0.1603373217,-4.7773294469
C,0.5570150042,0.0456175416,-1.2502772552
C,-1.4998537349,-0.2291306813,-4.2610671047
C,-0.2024438334,0.3002072138,3.1684905151
C,1.5203021797,-0.1607306993,4.537306167
C,-1.3659149154,-0.2996948758,-2.8661723
C,0.191681141,0.2295836005,4.5132287887
F,-2.598616501,-0.4937204543,-4.9530175171
F,-1.3920842398,0.6644183353,2.7076799529
F,-2.2992521134,-0.6632141194,-1.9961317182
F,-0.5709930143,0.4948081528,5.5640162141
H,-1.1048520713,0.0003151748,0.2129810566
H,0.0071048615,0.3606688859,-5.7992891874
H,2.1620620612,-0.3613551554,5.3811567354
H,2.5293450174,-0.4492873702,-1.691232996
H,2.9770768234,0.4473796243,0.629791159
H,1.4824450822,0.7732284483,-3.8182303295
H,2.7950535712,-0.7745799261,2.9936961556
N,1.9259014788,0.0914757887,-1.0783524276
N,2.1886836204,-0.0928849866,0.2852028336
N,0.6022384173,0.2857153333,-3.7366722125
N,1.9479122296,-0.2864906488,3.2451003715

Cartesian Coordination of 1e·H$^+$_2.

–1041.450356 hartree

C,-0.3954828323,0.0780702278,-2.5716784827
C,-0.4768318712,0.0553281145,-0.0289309331
C,0.4482569924,0.0228625033,2.3758413505
C,0.518035815,-0.036034764,0.9558355543
C,-0.5524511631,0.2169943748,-4.8208544486
C,0.1695152006,0.0481410348,-1.2664511554
C,-1.814224217,-0.0827840288,-4.3372731084
C,0.9646425518,0.1146641486,4.5861524286
C,-1.7214916775,-0.1609247497,-2.9386032324
C,-0.4164324573,0.164082963,4.4530384024
C,1.4995130799,0.024977928,3.2957615043
F,-2.9121312772,-0.2686279014,-5.0567697245
F,1.6483963552,0.1474331933,5.7211491671
F,-2.7023771014,-0.4530350849,-2.090049859
F,2.7911086171,-0.0313540251,2.9486831401
H,-1.5409300394,0.1428234555,0.1171167628
H,-0.2281526614,0.3933894437,-5.8345841929
H,-1.6504512711,0.1091328469,2.7530205126
H,-1.1771770356,0.2284768335,5.2152521413
H,2.1425450653,-0.5427145748,-1.6336497361
H,2.6084298556,0.0940751395,0.7311284105
H,1.219669265,0.7014152905,-3.8151051956
N,-0.7127958403,0.115009668,3.123865382
N,1.5281903591,0.0069069284,-1.040934501
N,1.7188703472,-0.1684561951,0.3214967976
N,0.3032781269,0.2824523721,-3.7554734632

Cartesian Coordination of 1e·H$^+$_3.

–1041.4532278 hartree

C,-0.8855177359,0.0154087987,-2.3985259589
C,-0.9169715171,0.000106584,0.190241437
C,0.1417233233,-0.015324767,2.55283868
C,0.1276042122,-0.0314899223,1.1258893741
C,-1.1485210031,-0.0524095914,-4.6540611345
C,-0.3308116866,0.0315311901,-1.0837307558
C,-2.4038087433,-0.0128174419,-4.0666161178
C,0.797718043,0.0524539524,4.7268411271
C,-0.587668538,0.0131837463,4.6872479847
C,-0.2071878837,-0.0335116375,-3.6162095187
C,1.2484877023,0.03336758,3.4001751314
F,-0.8852492944,-0.099991744,-5.9525499442
F,1.5558249541,0.0999246287,5.8134270177
F,1.1282508836,-0.0691819932,-3.7235610519
F,2.5164249428,0.0687218959,2.967411456
H,-1.9726564164,0.000213138,0.4092601189
H,-3.3787238602,-0.0069592947,-4.5281192095
H,-1.9273640787,-0.0775580153,3.0702400471
H,-2.989652819,0.0780486041,-2.0501173812
H,-1.2985326165,0.00753489,5.4984940272
H,1.7157684665,-0.1582621907,-1.606727497
H,2.2133651092,0.1578828143,0.7915613333
N,-0.9690231316,-0.0223898192,3.3770615738
N,-2.2324750479,0.0227350946,-2.7128560251
N,1.0188591427,0.0667009477,-0.9069011375
N,1.2955327227,-0.0669242205,0.4267412703

Cartesian Coordination of 2b_1.

–683.4995207 hartree

C,-0.8405990873,-2.5105139847,-0.0034755547
C,-0.8378795403,0.0781261087,-0.020927249
C,0.1602895425,2.445950828,-0.050261425
C,0.2069775745,0.9908571067,-0.0260784037
C,-0.8549155596,-4.7628847817,0.0146874913
C,-0.2245867392,-1.1959244672,-0.0147920579
C,-2.1709942768,-4.3439972852,0.0083700642
C,-0.6519692116,3.2952560947,-0.7844986722
C,0.6489933046,4.5696946173,0.5474328926
C,-2.1646954786,-2.9234400074,-0.003005259
C,-0.3422572804,4.629512084,-0.4088287867
C,2.7380895516,0.6951150423,-0.0862400443
N,1.1125432864,-1.0847303175,-0.0129874006
N,1.361062694,0.2460288614,-0.0277145581
N,-0.0612343273,-3.6457297533,0.007905114
N,0.9580685356,3.2469221338,0.7507122022
H,-1.8906046562,0.3137188395,0.0007667956
H,-0.4274256983,-5.7543442355,0.0234762883
H,-3.0395978074,-4.9871393003,0.0115689878
H,-1.3672222711,2.9761012654,-1.5288611539
H,1.1600778229,5.3511231639,1.0895567933
H,-3.0273249377,-2.2721682683,-0.0105419387
H,-0.7857767723,5.5323935513,-0.8036648123
H,3.3014857666,-0.0107844956,-0.6978774875
H,2.7796228158,1.6858368459,-0.5409041091
H,3.195411607,0.7320460468,0.9102600567
H,0.9463428471,-3.6126150402,0.0081565163
H,1.5632131663,2.9018870235,1.4783585871

Cartesian Coordination of 2b_2.

–683.5022884 hartree
C,-0.8034128109,-2.495398734,0.0128826552
C,-0.7695010443,0.0924403335,0.0382810829
C,0.2682687622,2.4456634214,0.0393768972
C,0.2903385266,0.993162712,0.044048952
C,-0.8441935416,-4.7474015998,0.0049008027
C,-0.171722018,-1.188191415,0.020761018
C,-2.1553113819,-4.3132568762,-0.0039678412
C,0.5381869839,4.6847784772,0.3031163128
C,-2.1322720543,-2.8927648173,0.0007643201
C,-0.6044395318,4.4730894831,-0.4394380797
C,1.0899658199,3.4117887967,0.6067922509
C,2.8131619158,0.6724616066,0.0088335846
N,-0.7628833846,3.1190475208,-0.5869160872
N,1.1660562552,-1.0922837625,0.0180259329
N,1.4312208534,0.2356718978,0.0222566091
N,-0.0376335934,-3.6395269509,0.0154278211
H,-1.8214431282,0.3308851769,0.087439267
H,-0.428117406,-5.7437257164,0.005290248
H,-3.0312717855,-4.946294552,-0.0127213692
H,0.9297126942,5.6462457651,0.602933785
H,-2.9874349486,-2.2315719697,-0.0037872916
H,-1.3075867208,5.1684760968,-0.872465719
H,1.9626512379,3.2181675898,1.2131185083
H,3.3965323261,-0.0805401681,-0.5217653352
H,2.8867800753,1.6318053643,-0.5056643377
H,3.2107357629,0.7793779339,1.0245664493
H,-1.4725865147,2.6667509466,-1.1409568093
H,0.9702897407,-3.6181657313,0.0243409381

Cartesian Coordination of 2b_3.
–683.4948988 hartree
C,-0.711967263,-2.3119522907,0.0345988002
C,-0.6939477099,0.2576299999,0.0017304314
C,0.3101529146,2.6423733284,-0.0002721474
C,0.3725435054,1.1904652654,0.0241059936
C,-1.0732399121,-4.4606258911,-0.564628773
C,-0.0945949023,-0.9938215063,0.0288379463
C,-2.0528237219,-4.1168936197,0.3426235355
C,0.6984661771,4.8738197014,-0.0937526861
C,-1.8281934586,-2.7660973272,0.7193655126
C,-0.6600308139,4.6800555639,0.0526610662
C,1.3105349617,3.5934481788,-0.1269360949
C,2.345816232,-1.712902554,0.1569892225
N,-0.8850132094,3.3263636792,0.1042242693
N,1.2566499123,-0.7592691827,0.068822626
N,1.5551469548,0.5600752279,0.0611151279
N,-0.258547001,-3.368643237,-0.7377450802
H,-1.7560332278,0.4405211639,-0.0684035406
H,-0.8857918329,-5.3847983737,-1.0904106318
H,-2.8350073099,-4.7684388292,0.7052252983
H,1.195035848,5.8307636595,-0.1711684114
H,-2.3939520528,-2.1854015125,1.4337502138
H,-1.4751516295,5.384539888,0.1229712395
H,2.3611726995,3.3694809308,-0.2369335504
H,1.9946136021,-2.6268815208,0.6383066655
H,3.1385853931,-1.2638253874,0.7558784504
H,2.7536480034,-1.9546124843,-0.8322528201
H,-1.7834052987,2.8940609514,0.243498739
H,0.4723331538,-3.2980869905,-1.4273170941

Cartesian Coordination of 2b_4.
–683.4970747 hartree
C,-0.6677392295,-2.551952272,0.0017219184
C,-0.676757349,0.0359463421,0.027702023
C,0.3119181187,2.4122177016,0.0353971093
C,0.3629163017,0.9602334559,0.0460793251
C,-1.1680664757,-4.760045425,-0.1139814906
C,-0.0518957098,-1.2353909163,0.0215486606
C,-2.3383802686,-4.0666025092,0.116766206
C,0.5311094747,4.6563331385,0.3035872663
C,-0.5778937948,4.4231719549,-0.4819169566
C,-0.1160840037,-3.8094234613,-0.1857316907
C,1.0936074023,3.3938097658,0.6312054257
C,2.8903165346,0.6871262732,0.0466082125
N,-0.7072948542,3.0657545224,-0.6309925665
N,-2.0261053699,-2.7303049891,0.1786875758
N,1.2823052368,-1.1084763932,0.0372739598
N,1.5161745162,0.22371244,0.0387901267
H,-1.7322853797,0.2677019292,0.0428843395
H,-1.0802975676,-5.8318340309,-0.2228628626
H,-3.3550993515,-4.408548588,0.2394374746
H,0.8933673051,5.6251625574,0.6162495462
H,-1.2754254726,5.105272252,-0.9441870892
H,0.9319108606,-4.0005062372,-0.362543135
H,1.946057965,3.2163587635,1.2704507089
H,3.493769623,-0.0533121545,-0.4786675849
H,2.9526400468,1.6508080154,-0.4610852976
H,3.2701614114,0.7945826377,1.0687105665
H,-1.3798555864,2.6009863732,-1.2198370343
H,-2.678806561,-1.9940148676,0.391220643

Cartesian Coordination of 2c_1.
–1080.3856791 hartree
C,-0.3000106687,-2.5804091324,0.0929742779
C,-0.2840655773,-0.0028900144,0.0909398495
C,0.7146091604,2.3498706292,0.1085687637
C,0.7685305749,0.9016316724,0.1280403091
C,-0.3934279004,-4.8460531746,0.0829081519
C,0.326716114,-1.2758765284,0.1124257581
C,-1.6876551807,-4.3701713432,0.0537716595
C,-0.2395795343,3.1697443334,-0.4713830813
C,1.250689325,4.516658681,0.5548765914
C,-1.6315196561,-2.9588552894,0.0603328783
C,0.0976184406,4.5137266824,-0.1959366405
C,3.3018092389,0.5895217075,0.1619760999
F,-2.8066604377,-5.1079892357,0.024691425
F,-1.2895301073,2.7579205411,-1.1914573524
F,-2.6821881246,-2.1223167362,0.0398773155
F,-0.5797708153,5.58736922,-0.6181598508
N,1.6629384064,-1.1771945947,0.1588439476
N,1.9196398107,0.1524857116,0.1561391811
N,0.4307086576,-3.747603439,0.1067573479
N,1.627568976,3.2014148691,0.7137354237
H,-1.3362634637,0.2284228929,0.0559440937
H,-0.0211286052,-5.8572723936,0.0872817487
H,1.8176741614,5.3364210031,0.96445995
H,3.8987141311,-0.1943290022,-0.3040851748
H,3.4025813177,1.5124528841,-0.4121359
H,3.6761698833,0.7487075888,1.1815123113

H,1.4380150458,-3.7509920192,0.1285954356
H,2.319305921,2.8966277728,1.3785646918

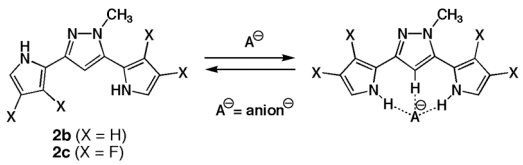
Cartesian Coordination of 2c_2.
–1080.3899051 hartree
C,-0.5616995911,0.1128100147,-2.6128289341
C,-0.5616782537,0.1048825069,-0.0373827396
C,0.4432739346,0.0973856641,2.3237365566
C,0.4876262951,0.0714358951,0.8738124041
C,-0.6539578385,0.0993270772,-4.8782461542
C,0.0589741497,0.0961059618,-1.3056836014
C,-1.9477241607,0.1595355765,-4.4039246339
C,0.6426696366,-0.2093864875,4.5649072432
C,-1.8919141673,0.1678894567,-2.9927754317
C,-0.4080511056,0.6566888159,4.3576939244
C,1.1697691842,-0.5630951918,3.3032721576
C,3.0167278947,0.0314229937,0.5990124081
F,-3.0658212758,0.2033196524,-5.1424449313
F,1.0865159727,-0.657844274,5.7454731972
F,-2.9420900133,0.2222059865,-2.1543562237
F,2.1757304438,-1.4273815655,3.0938870707
H,-1.6192825203,0.0925031517,0.1750989159
H,-0.2809946395,0.0740418408,-5.888918396
H,-1.0544416963,1.1539826078,5.062085126
H,3.6367111027,0.4411023043,-0.1976593497
H,3.1118148414,0.6467979595,1.4956263272
H,3.3408003312,-0.9858154201,0.8333529298
H,-1.1482784935,1.4646353049,2.5421194375
H,1.1755936688,0.0231622284,-3.7811543561
N,-0.5207433704,0.8228677809,2.9991394391
N,1.3946055985,0.0590125636,-1.1944344728
N,1.6405794836,0.0567138142,0.1350241993
N,0.1691247727,0.0723884311,-3.7787494295

Cartesian Coordination of 2c_3.
–1080.3792615 hartree
C,-0.5473024773,-2.4734341782,-0.0378089018
C,-0.5349541052,0.0777175531,-0.0521268522
C,0.4303554321,2.4635817905,-0.023984589
C,0.5245266734,1.0158994925,-0.0234786671
C,-0.8672873715,-4.6995552671,-0.3881500359
C,0.079246953,-1.1678612184,-0.0362524366
C,-2.02544741,-4.1883095924,0.1520821528
C,0.7413755671,4.7058546761,-0.1522333931
C,-1.8303472298,-2.8070384937,0.3677390105
C,-0.5827992196,4.4920405229,0.1585726066
C,1.3756640332,3.4478813892,-0.265207348
C,2.5336060648,-1.8598078027,0.0629379838
F,-3.1371473808,-4.872589119,0.4452650952
F,1.33416294,5.8945600238,-0.331719222
F,-2.7270067599,-1.9596518855,0.892220973
F,2.6608329449,3.2541591972,-0.5796263389
N,-0.7574418512,3.129023281,0.2171631173
N,1.4282648061,-0.922958553,0.0062280773
N,1.7138621372,0.4002017531,0.0083214413
N,0.0254527843,-3.655445597,-0.4806087704
H,-1.5984987786,0.2517022085,-0.1071775929
H,-0.6203828648,-5.7029456963,-0.6936770768
H,-1.3838106217,5.1907377445,0.3352101322
H,2.2928495798,-2.6896556592,0.7314517983
H,3.3948148481,-1.3180064718,0.4520043876
H,2.7912374575,-2.2475513041,-0.9312958482
H,-1.5968415322,2.6750776011,0.5371128753
H,0.8922696172,-3.7052217912,-0.9891574801

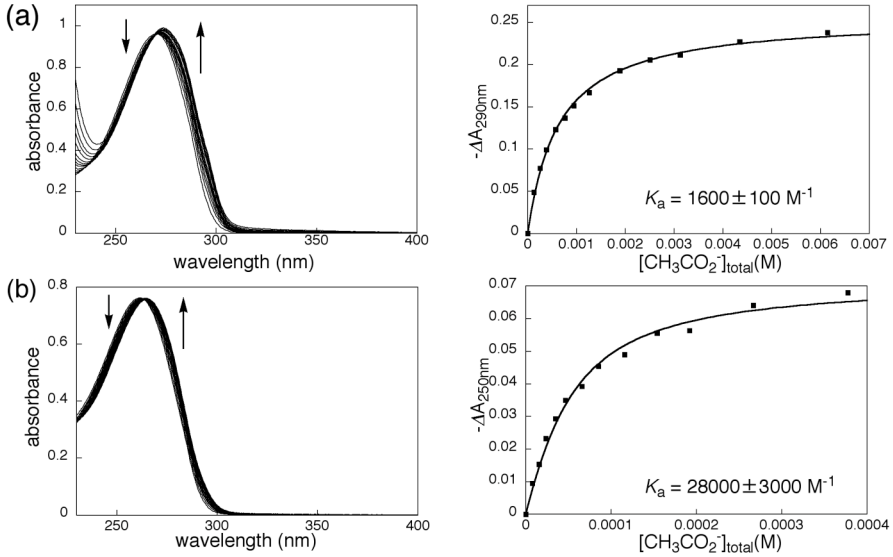
Cartesian Coordination of 2c_4.
–1080.3817235 hartree
C,-0.8182124438,0.0695442165,-2.4888933207
C,-0.8359293816,0.0584487925,0.0878978295
C,0.1406599481,0.0432946029,2.4651898661
C,0.1989244875,0.0117656257,1.0154994933
C,-1.3620988261,0.2817426866,-4.6797450043
C,-0.1987851945,0.0426037857,-1.1765736026
C,-2.4892436547,-0.1490742604,-4.0180528455
C,0.3177123489,-0.2645399873,4.7080522708
C,-0.694323404,0.6444175588,4.4946113751
C,-0.3198778676,0.4169596419,-3.7335432718
C,0.8349881281,-0.6434983084,3.4491384688
C,2.7284546847,-0.0529793932,0.7712607198
F,-1.2613917931,0.5482745978,-5.9892381396
F,0.7345541944,-0.7314364288,5.8911158466
F,0.9173254144,0.8463357174,-4.00189535
F,1.8031130771,-1.5507467099,3.2460625887
H,-1.8929252339,0.091523433,0.3094002188
H,-3.4749040653,-0.3795122297,-4.3874535651
H,-1.3203268215,1.1720434189,5.1953342325
H,3.3649679759,0.2831244265,-0.0458355113
H,2.8369753577,0.6156002012,1.6280019558
H,3.0136639638,-1.0634792284,1.0731249898
H,-1.3702978825,1.4995840395,2.6767573555
H,-2.7205664846,-0.7006120502,-1.991015132
N,-0.7980379456,0.8083086676,3.1341201834
N,-2.1494973038,-0.2513112981,-2.6877419306
N,1.133802304,-0.0121053419,-1.0414009488
N,1.3576461176,-0.0137815084,0.2890554208

[S4] *Gaussian 03*, (Revision C.01), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford CT, 2004.

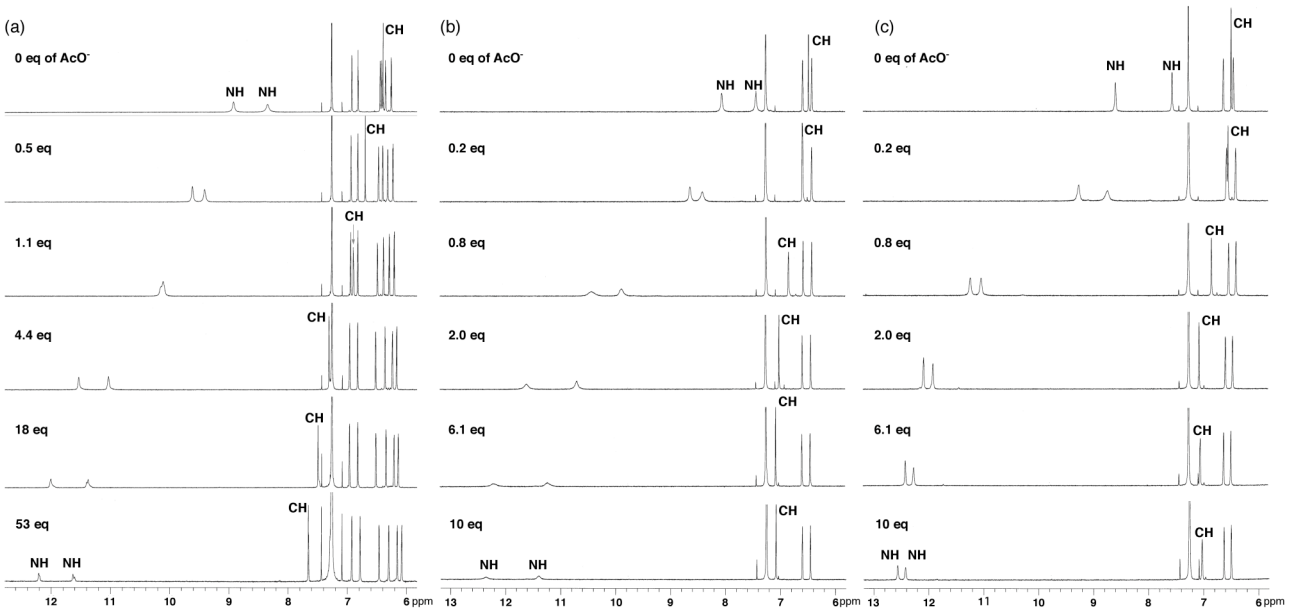
4. Anion binding properties of N-methyl-substituted dipyrrolylpyrazoles



Supporting Figure 6 Schematic representation of possible anion binding mode of N-methyl-substituted dipyrrolyldiketones **2b** and **2c**.

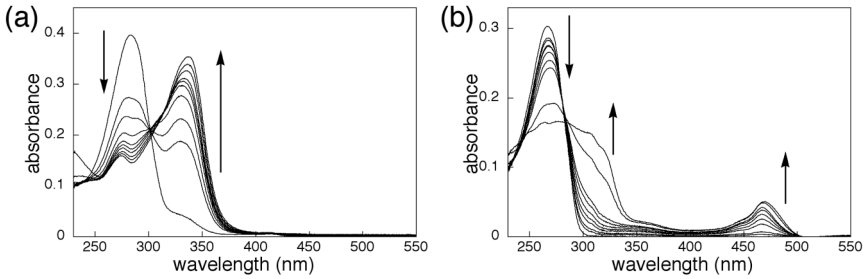


Supporting Figure 7 UV/vis absorption spectral changes (left) and corresponding titration plots and 1:1 fitting curves (right) of (a) **2b** (3.2×10^{-5} M) and (b) **2c** (3.2×10^{-5} M) upon the addition of $CH_3CO_2^-$ as a tetrabutylammonium salt in CH_2Cl_2. As the absorption maxima in both cases are also isosbestic points, absorption spectral changes at the alternative wavelengths were used instead.

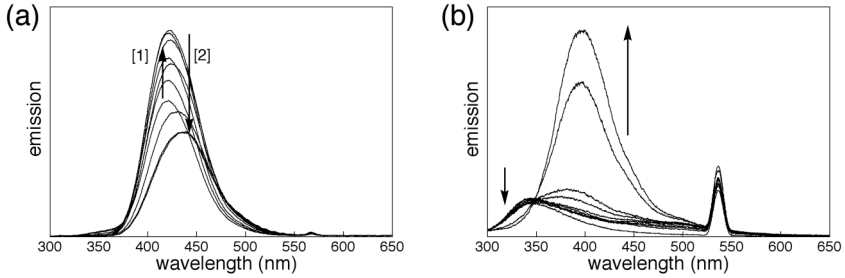


Supporting Figure 8 ^{1}H NMR spectral changes in $CDCl_3$ of (a) **2b** (3.1×10^{-3} M) at r.t. and **2c** (3.1×10^{-3} M) at (b) r.t. and (c) –50 °C upon the addition of $CH_3CO_2^-$ (0–53 and 0–10 equiv for **2b** and **2c**, respectively) as a tetrabutylammonium salt. In sharp contrast to BF_2 complexes of dipyrrolyldiketones, resonances ascribable to the anion-free and binding species of **2b**,**c** are coalesced to a single pair of signals, inferring the fast exchanges between them, possibly due to the "semi-preorganized" conformation, with one *inverted* pyrrole ring as shown in Supporting Figures 5 and 6, suggested by DFT calculations and low barrier of pyrrole ring's rotation.

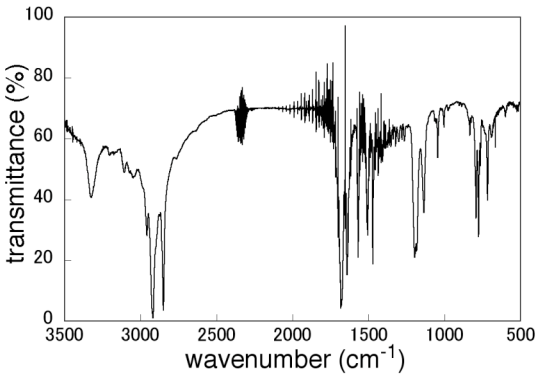
5. Spectral changes of dipyrrolylpyrazoles by TFA addition



Supporting Figure 9 UV/vis absorption spectral changes of (a) **1d** (1.0×10^{-5} M) and (b) **1e** (1.0×10^{-5} M) upon the addition of TFA (0–940 equiv. for **1d** and 0–24, 106, and 189 equiv. for **1e**) in CH_2Cl_2.



Supporting Figure 10 Fluorescence spectral changes of (a) **1d** (1.0×10^{-5} M) and (b) **1e** (1.0×10^{-5} M) upon the addition of TFA (0–940 equiv. for **1d** and 0–24, 106, and 189 equiv. for **1e**) in CH_2Cl_2.



Supporting Figure 11 IR spectroscopy diagram of **1d**·TFA (KBr).