Supporting Information

Assembly of Robust Two Dimensional Sheet Structures from Crystalline Ring-Fused Malonamides via Cooperative Hydrogen Bonding of Amide Groups

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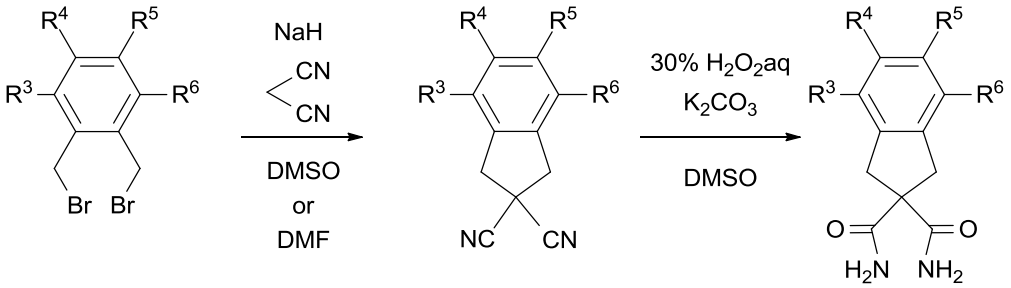
Experimental procedures

General remarks

^{1}H and ^{13}C NMR spectra were recorded on a JEOL AL-300 (^{1}H/300 MHz, ^{13}C/75 MHz), Bruker BioSpin・Avance DPX-300 (^{1}H/300 MHz, ^{13}C/75 MHz), Bruker Biospin・AVANCE DPX-400 (^{1}H/400 MHz, ^{13}C/100 MHz) or Bruker Biospin・AVANCE 400M (^{1}H/400 MHz, ^{13}C/100 MHz) spectrometers. The chemical shifts of the ^{1}H and ^{13}C NMR signals are quoted relative to TMS in $CDCl_3$ unless otherwise indicated. IR spectra were taken on a JASCO model FT/IR-230 and HORIBA FT-710 infrared spectrophotometers. Mass spectra were recorded on a JEOL JMS-600H (EI, 70eV), JMS-AX505H (FAB), JMS-SX102A (FD) and JMS-T100GCv (FD) spectrometers. Column chromatography was performed on silica gel 60 (Merck, particle size 63-200 μm) and aluminum oxide 90 (Merck, 63-200 μm), respectively. Melting points were measured on a Yamato MP-21 apparatus. Elemental analyses were taken on a Yanako MT-6 CHN corder at the Center for Instrumental Analysis of Hokkaido University. Solvents were purified prior to use. Reactions were carried out under an argon atmosphere unless otherwise indicated. 1,2-Bis(bromomethyl)-4,5-dimethoxybenzene **3c**,[S3] 2,3-bis(bromomethyl)-1,4-dimethoxybenzene **3d**,[S4] 1,8-bis(bromomethyl)naphthalene **3f**,[S5] and 2,2-indanedicarbonitrile **4a**[S1] were prepared following the known procedures.



3a : R^{3-6} = H
3b : R^4 = I, $R^{3,5,6}$ = H
3c : $R^{3,6}$ = H, $R^{4,5}$ = OMe
3d : $R^{3,6}$ = OMe, $R^{4,5}$ = H

4a : R^{3-6} = H
4b : R^4 = I, $R^{3,5,6}$ = H
4c : $R^{3,6}$ = H, $R^{4,5}$ = OMe
4d : $R^{3,6}$ = OMe, $R^{4,5}$ = H

1a : R^{3-6} = H
1b : R^4 = I, $R^{3,5,6}$ = H
1c : $R^{3,6}$ = H, $R^{4,5}$ = OMe
1d : $R^{3,6}$ = OMe, $R^{4,5}$ = H

2,2-Indanedicarbonitrile 4a

To a suspension of NaH (228 mg, 9.5 mmol) in dry DMSO (22 mL) was added malononitrile (275 mg, 4.2 mmol) at 25 °C. After gas evolution ceased, *o*-xylylene dibromide **3a** (1.02 g, 3.86 mmol) was added and the resulting suspension was heated at 50 °C for 2 h. After cooling, the mixture was neutralized with 0.1 M HClaq and extracted with chloroform (× 2). The organic layer was washed with 0.1 M HClaq, water and brine, dried over $MgSO_4$ and then filtered. The brown solid obtained by evaporation of the solvent was subjected to chromatography on SiO_2 eluting with ether to give **4a** (548 mg, 85%) as a beige solid: The spectral data were identical with those reported in the literature.[S1] ^{1}H NMR ($CDCl_3$): δ/ppm 7.31 (s, 4H), 3.74 (s, 4H).

2,2-Indanedicarboxamide 1a

To a solution of dinitrile **4a** (548 mg, 3.26 mmol) in DMSO (3.0 mL) was added 30% H_2O_2aq (1.2 mL). After cooling to 0 °C, K_2CO_3 (200 mg, 1.45 mmol) was added portionwise and stirred at 25 °C for 1 h. The resulting suspension was diluted with water and filtered. The filtered solid was washed with H_2O to give **1a** (283 mg, 43%) as a white solid. Crystals for X-ray structural analysis were obtained by recrystallizing from THF: m.p. 258-260 °C (dec.); ^{1}H NMR (DMSO-d_6): δ/ppm 7.18-7.06 (m, 8H), 3.39 (s, 8H); ^{13}C NMR (DMSO-d_6): δ/ppm: 173.21, 141.03, 126.24, 123.88, 62.00, 39.86; IR (KBr): ν/cm^{-1} 3447, 3359, 3201, 2958, 2917, 1689, 1655, 1623, 1591, 1404, 1355, 1134, 1099, 942, 863, 784, 670; MS (EI) *m/z* (%): 204 (M^+, 16), 160 (77), 143 (29), 117 (50), 116 (74), 115 (BP); HR-MS (EI) Calcd. for $C_{11}H_{12}N_2O_2$: 204.0899; found: 204.0906; Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72; found: C, 64.62; H, 5.99; N, 13.67.

1,2-Bis(bromomethyl)-4-iodobenzene 3b

The mixture of 4-iodoxylene (3.48 g, 15.0 mmol), NBS (5.90 g, 33.0 mmol) and benzoyl peroxide (180 mg, 0.75 mmol) in benzene (94 mL) was refluxed for 20 h. After cooling to r.t., the resulting suspension was filtered to remove succinimide and unreacted NBS. The filtrate was washed with 5% $Na_2S_2O_3$aq, water and brine, dried over $MgSO_4$ and then filtered. The yellow oil obtained by evaporation of the solvent was subjected to chromatography on SiO_2 eluting with hexane to give **3b** (2.95 mg, 50%) as a white solid. The spectral data were identical with those reported in the literature.[S2] ^{1}H NMR ($CDCl_3$): δ/ppm 7.72 (d, *J* = 1.7 Hz, 1H), 7.64 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 4.58 (s, 2H), 4.56 (s, 2H).

5-Iodoindane-2,2-dicarbonitrile 4b

To a suspension of NaH (60% in oil, 230 mg, 5.7 mmol) and 1,2-bis(bromomethyl)-4-iodobenzene **4b**[S2] (999 mg, 2.58 mmol) in dry DMF (2.6 mL) was added a solution of malononitrile (193 mg, 2.91 mmol) in DMF (2.6 mL) dropwise at 25 °C over 1 h. After gas evolution ceased, the resulting suspension was stirred for 1 h. The mixture was poured into a separating funnel containing EtOAc and water, and neutralized with 1 M HClaq and extracted with EtOAc (× 2). The organic layer was washed with 1 M HClaq, water and brine, dried over $MgSO_4$ and then filtered. The red solid obtained by evaporation of the solvent was subjected to chromatography on SiO_2 eluting with EtOAc/hexane (1/19) to give **4b** (263 mg, 35%) as a pale yellow solid: m.p. 140-141 °C (dec.); ^{1}H NMR ($CDCl_3$): δ/ppm 7.67 (s, 1H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 3.71 (s, 2H), 3.68 (s, 2H); ^{13}C NMR ($CDCl_3$): δ/ppm: 138.65, 137.80, 135.97, 133.99, 126.54, 115.83, 93.73, 44.14 (2C), 33.66; IR (KBr): ν/cm^{-1} 2985, 2938, 2254, 2245, 1476, 1430, 1289, 1268, 1250, 1237, 1172, 1091, 1031, 889, 870, 811, 733; MS (FAB+) *m/z* (%): 293.6 (M^+).

5-iodoindane-2,2-dicarboxamide 1b

To a solution of dinitrile **4b** (101 mg, 0.34 mmol) in DMSO (1.0 mL) was added 30% H_2O_2aq (0.3 mL) at 0 °C. To a solution was added K_2CO_3 (42 mg, 0.30 mmol) and stirred at 25 °C for 30 min. The resulting suspension was diluted with 1 M HClaq and filtered. The filtered solid was washed with H_2O to give **1b** (75 mg, 67%) as a white solid. Crystals for X-ray structural analysis were obtained by recrystallizing from CH_3CN: m.p. 273-274 °C (dec.); ^{1}H NMR (acetone-d_6): δ/ppm 7.56 (s, 1H), 7.48 (d, J = 8.7 Hz, 1H), 7.03 (d, J = 7.9 Hz, 1H), 6.89 (br.s, 2H), 6.53 (br.s, 2H), 3.55 (s, 2H), 3.51 (s, 2H); ^{13}C NMR (DMSO-d_6): δ/ppm: 172.78, 144.19, 140.98, 134.89, 132.54, 126.20, 91.53, 61.90, 40.09-38.84 (overlapped with solv.); IR (KBr): 3360, 3174, 2963, 2916, 1645, 1628, 1595, 1365, 1228, 1178, 1133, 1103, 1069, 877, 813, 781, 721, 656 cm^{-1}; MS (FAB+) *m/z* (%): 330.5 (M^+).

5,6-Dimethoxyindane-2,2-dicarbonitrile 4c

To a suspension of NaH (101 mg, 4.2 mmol) in dry DMSO (5 mL) was added a solution of 1,2-bis(bromomethyl)-4,5-dimethoxybenzene **3c**[S3] (648 mg, 2.0 mmol) and malononitrile (132 mg, 2.0 mmol) in dry DMSO (4 mL) dropwise at 0 °C over 5 min. After stirring the resulting suspension at 25 °C for 2 h, the mixture was poured into a separating funnel containing EtOAc and water, and neutralized with 0.1 M HClaq and extracted with EtOAc (× 2). The organic layer was washed with 0.1 M HClaq, 5% $NaHCO_3$aq and brine, dried over $MgSO_4$ and then filtered. The orange solid obtained by evaporation of the solvent was subjected to chromatography on SiO_2 eluting with EtOAc/hexane (4/6) to give **4c** (344 mg, 75%) as a white solid: m.p. 119.5-120.5 °C; ^{1}H NMR ($CDCl_3$): δ/ppm 6.78 (s, 2H), 3.88 (s, 6H), 3.67 (s, 4H); ^{13}C NMR ($CDCl_3$): δ/ppm: 149.84, 127.96, 116.44, 107.44, 56.14, 44.76, 33.97; IR (KBr): 2964, 2939, 2835, 2244, 1610, 1504, 1466, 1319, 1278, 1245, 1222, 1097, 989, 859, 722, 570 cm^{-1}; MS (EI) *m/z* (%): 229 (M^++1, 26), 228 (M^+, BP), 213 (45), 158 (34); HR-MS (EI) Calcd. for $C_{13}H_{12}N_2O_2$: 228.0899; found: 204.0898.

5,6-Dimethoxyindane-2,2-dicarboxamide 1c

To a solution of **4c** (237 mg, 1.04 mmol) in dry DMSO (5.0 mL) was added 30% H_2O_2aq (4.0 mL). After cooling to r.t., K_2CO_3 (250 mg, 1.81 mmol) was added portionwise and stirred at 25 °C for 3 h. The resulting suspension was diluted with water and filtered. The filtered solid was washed with EtOH to give **1c** (115 mg, 42%) as a white solid. Crystals for X-ray structural analysis were obtained by recrystallizing from CH_3CN/benzene: m.p. 260-263 °C (dec.); ^{1}H NMR (DMSO-d_6): δ/ppm 7.12 (br.s, 2H), 7.10 (br.s, 2H), 6.77 (s, 2H), 3.70 (s, 6H), 3.32 (s, 4H); ^{13}C NMR (DMSO-d_6): δ/ppm: 173.35, 147.84, 132.43, 108.07, 62.50, 55.60; IR (KBr): 3413, 3366, 3308, 3192, 2928, 2830, 1660, 1624, 1509, 1465, 1324, 1274, 1218, 1094, 994, 850, 837 cm^{-1}; MS (EI) *m/z* (%): 264 (M^+, 80), 220 (BP), 219 (50), 203 (29); HR-MS (EI) Calcd. for $C_{13}H_{16}N_2O_4$:

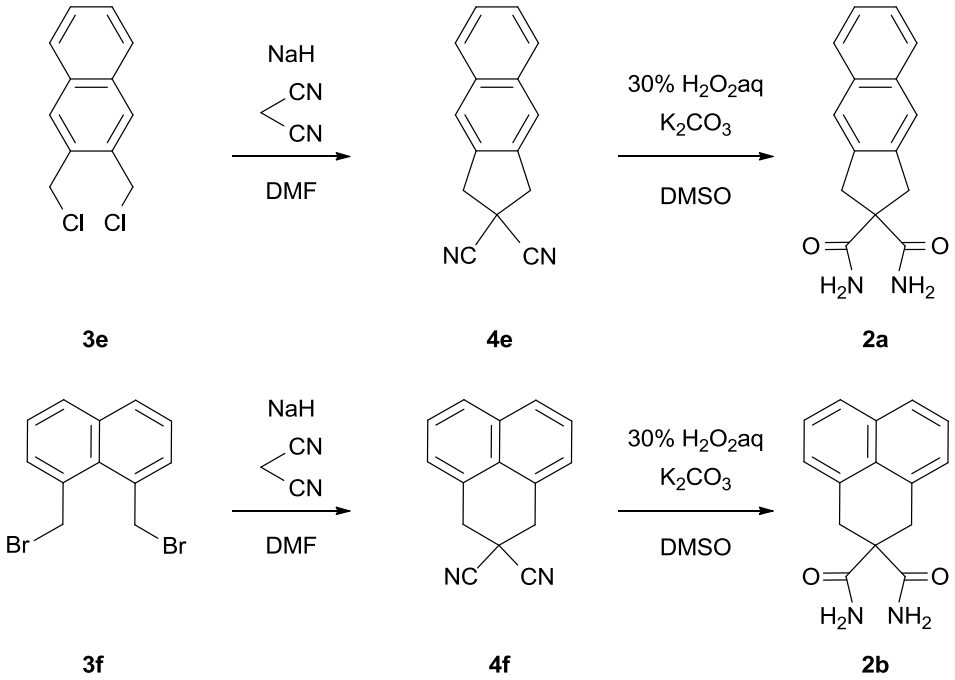
264.1110; found: 264.1137; Anal. Calcd. for $C_{13}H_{16}N_2O_4 \cdot 0.5H_2O$: C, 57.13; H, 6.27; N, 10.25; found: C, 56.89; H, 6.10; N, 10.00.

4,7-Dimethoxyindane-2,2-dicarbonitrile 4d

To a suspension of NaH (101 mg, 4.2 mmol) in dry DMSO (5 mL) was added a suspension of 2,3-bis(bromomethyl)-1,4-dimethoxybenzene **3d**[S4] (648 mg, 2.0 mmol) and malononitrile (132 mg, 2.0 mmol) in dry DMSO (4 mL) at 25 °C. After stirring the resulting suspension for 2 h, the mixture was diluted with EtOAc and water and filtered. The filtrate was washed with 0.1 M HClaq, 5% $NaHCO_3$aq and brine, dried over $MgSO_4$ and then filtered. The yellow oil obtained by evaporation of the solvent was subjected to chromatography on SiO_2 eluting with EtOAc/hexane (2/8) to give **4d** (92 mg, 20%) as a white solid: m.p. 172-173 °C; ^{1}H NMR ($CDCl_3$): δ/ppm 6.72 (s, 2H), 3.79 (s, 6H), 3.69 (s, 4H); ^{13}C NMR ($CDCl_3$): δ/ppm: 149.88, 125.87, 116.52, 110.77, 55.62, 42.51, 33.28; IR (KBr): 2968, 2943, 2839, 2254, 1504, 1440, 1266, 1085, 958, 812, 716, 655 cm^{-1}; MS (EI) *m/z* (%): 229 (M^++1, 15), 228 (M^+, BP), 213 (94); HR-MS (EI) Calcd. for $C_{13}H_{12}N_2O_2$: 228.0899; found: 204.0926.

4,7-Dimethoxyindane-2,2-dicarboxamide 1d

To a suspension of **4c** (53 mg, 0.23 mmol) in dry DMSO (2.0 mL) was added 30% H_2O_2aq (1.0 mL) and K_2CO_3 (80 mg, 0.58 mmol) and stirred at 25 °C for 1 h. The resulting suspension was diluted with water and filtered. The filtered solid was washed with water to give **1d** as a white solid. Crystals for X-ray structural analysis were obtained by recrystallizing from THF: m.p. 273-274 °C (dec.); ^{1}H NMR (DMSO-d_6): δ/ppm 7.14 (br.s, 2H), 7.11 (br.s, 2H), 6.67 (s, 2H), 3.70 (s, 6H), 3.33 (s, 4H); ^{13}C NMR (DMSO-d_6): δ/ppm: 173.24, 149.27, 129.89, 109.07, 61.55, 55.24; IR (KBr): 3413, 3302, 3213, 2999, 2965, 2894, 2832, 1653, 1615, 1492, 1462, 1360, 1252, 1136, 1084, 1054, 960, 809, 653, 600 cm^{-1}; MS (EI) *m/z* (%): 264 (M^+, 50), 220 (BP), 219 (30), 203 (33), 176 (46), 161 (49); HR-MS (EI) Calcd. for $C_{13}H_{16}N_2O_4$: 264.1110; found: 264.1140; Anal. Calcd. for $C_{13}H_{16}N_2O_4$: C, 59.08; H, 6.10; N, 10.60; found: C, 58.94; H, 6.13; N, 10.57.



1,3-Dihydrocyclopenta[*c*]napthalene-2,2-dicarbonitrile 4e

To a suspension of NaH (60% in oil, 135 mg, 3.4 mmol) and 2,3-bis(chloromethyl)naphthalene **3e** (299 mg, 1.33 mmol) in dry DMF (3.0 mL) was added a solution of malononitrile (142 mg, 2.14 mmol) in DMF (2.0 mL) dropwise at 25 °C over 1 h. After gas evolution ceased, the resulting suspension was stirred for 1 h. The mixture was poured into a separating funnel containing EtOAc and water, and neutralized with 1 M HClaq and extracted with EtOAc (× 2). The organic layer was washed with 1 M HClaq, water and brine, dried over $MgSO_4$ and then filtered. The pale yellow solid obtained by evaporation of the solvent was subjected to chromatography on SiO_2 eluting with $CHCl_3$/hexane (1/1) to give **4e** (139 mg, 42%) as a pale yellow solid: m.p. 216-217 °C; ^{1}H NMR ($CDCl_3$): δ/ppm 7.82 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.77 (s, 2H), 7.50 (dd, *J* = 6.6, 3.3 Hz, 2H), 3.86 (s, 4H); ^{13}C NMR ($CDCl_3$): δ/ppm: 134.16, 133.40, 127.89, 126.60, 123.85, 116.10, 44.25, 34.32; IR (KBr): ν/cm^{-1} 3051, 2970, 2923, 2257, 2248, 1500, 1435, 1087, 1023, 907, 872, 766, 483; MS (EI) *m/z* (%): 218 (M^+, bp), 190 (35); HR-MS (EI) Calcd. for $C_{15}H_{10}N_2$: 218.0844; found: 218.0856.

1,3-Dihydrocyclopenta[*c*]napthalene-2,2-dicarboxamide 2a

To a solution of dinitrile **4e** (110 mg, 0.50 mmol) in DMSO (2.0 mL) was added 30% H_2O_2aq (0.5 mL) at 0 °C. To a solution was added K_2CO_3 (36 mg, 0.22 mmol) and stirred at 25 °C for 30 min. The resulting suspension was diluted with 1 M HClaq and filtered. The filtered solid was washed with EtOH to give **2a** (80 mg, 63%) as a white solid. Crystals for X-ray structural analysis were obtained by recrystallizing from THF: m.p. 270-272 °C (dec.); ^{1}H NMR (DMSO-d_6): δ/ppm 7.79 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.66 (s, 2H), 7.39 (dd, *J* = 6.6, 3.3 Hz, 2H), 7.22 (br.s, 2H), 7.16 (br.s, 2H), 3.53 (s, 4H); ^{13}C NMR (DMSO-d_6): δ/ppm: 172.94, 140.45,

132.51, 127.27, 124.96, 121.71, 62.45, 40.33-38.67 (overlapped with solv.); IR (KBr): 3450, 3360, 3206, 1690, 1662, 1651, 1352, 1124, 1083 cm^{-1}; MS (EI) *m/z* (%): 254 (M^+, 80), 211 (35), 210 (BP), 209 (34), 193 (50), 167 (29), 166 (67), 165 (76); Anal. Calcd. for $C_{15}H_{10}N_2O_2 \cdot 0.2EtOH$: C, 70.20; H, 5.81; N, 10.63; found: C, 70.10; H, 5.53; N, 10.38.

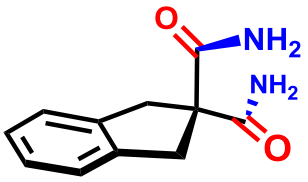
1,3-Dihydrophenalene-2,2-dicarbonitrile 4f

To a suspension of NaH (60% in oil, 36 mg, 0.90 mmol) and 1,8-bis(bromomethyl)naphthalene **3f**[S5] (103 mg, 0.33 mmol) in dry DMF (3.0 mL) was added a solution of malononitrile (38 mg, 0.58 mmol) in DMF (2.0 mL) dropwise at 25 °C over 1 h. After gas evolution ceased, the resulting suspension was stirred for 1 h. The mixture was poured into a separating funnel containing EtOAc and water, and neutralized with 1 M HClaq and extracted with EtOAc (× 2). The organic layer was washed with 1 M HClaq, water and brine, dried over $MgSO_4$ and then filtered. The red solid obtained by evaporation of the solvent was subjected to chromatography on SiO_2 eluting with $CHCl_3$/hexane (1/1) to give **4f** (42 mg, 55%) as a white solid: m.p. 210.0-210.5 °C; ^{1}H NMR ($CDCl_3$): δ/ppm 7.84 (d, *J* = 8.1 Hz, 2H), 7.49 (dd, *J* = 8.1, 7.2 Hz, 2H), 7.37 (d, *J* = 6.9 Hz, 2H), 3.79 (s, 4H); ^{13}C NMR ($CDCl_3$): δ/ppm: 133.44, 128.48, 127.50, 126.52, 126.13, 125.91, 115.35, 39.50, 30.61; IR (KBr): ν/cm^{-1} 2924, 2252, 1597, 1512, 1396, 1088, 825, 779; MS (EI) *m/z* (%): 218 (M^+, BP), 190 (37), 153 (22); HR-MS (EI) Calcd. for $C_{15}H_{10}N_2$: 218.0844; found: 218.0843.

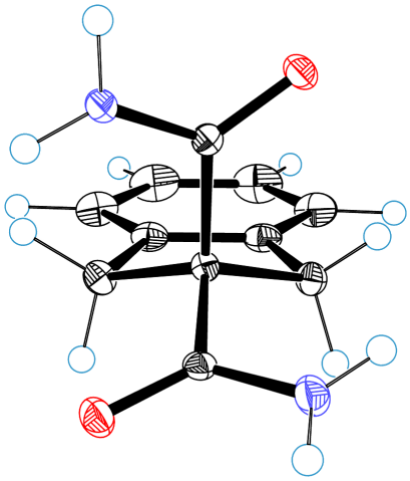
1,3-Dihydrophenalene-2,2-dicarboxamide 2b

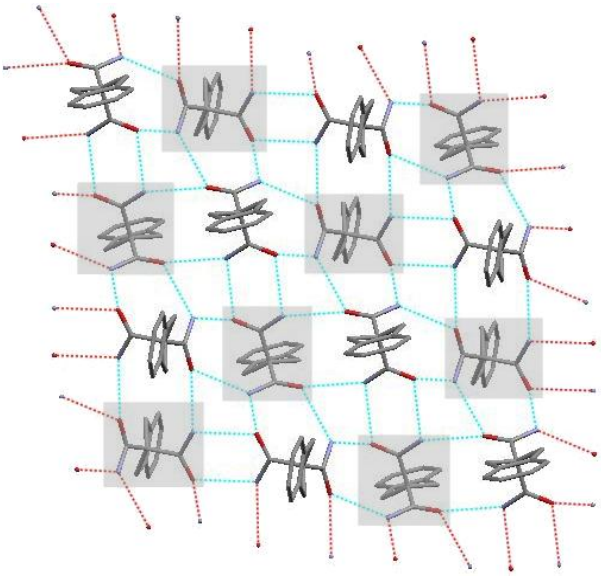
To a solution of dinitrile **4f** (69 mg, 0.32 mmol) in DMSO (1.0 mL) was added 30% H_2O_2aq (0.2 mL) at 0 °C. To a solution was added K_2CO_3 (26 mg, 0.18 mmol) and stirred at 25 °C for 30 min. The resulting suspension was diluted with 1 M HClaq and filtered. The filtered solid was washed with water to give **2b** (47 mg, 57%) as a white solid. Crystals for X-ray structural analysis were obtained by recrystallizing from THF: m.p. 284-285 °C (dec.); ^{1}H NMR ($CDCl_3$): δ/ppm 7.73 (d, *J* = 8.3 Hz, 2H), 7.42 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.33 (d, *J* = 6.9 Hz, 2H), 6.50 (br.s, 2H), 5.34 (br.s, 2H), 3.69 (s, 4H); ^{13}C NMR (DMSO-d_6): δ/ppm: 172.43, 134.10, 132.78, 128.64, 125.62, 125.53, 124.25, 53.56, 35.97; IR (KBr): 3440, 3397, 1657, 1646, 1392, 1363, 1221, 1174, 1141, 819, 814, 770 cm^{-1}; MS (EI) *m/z* (%): 254 (M^+, 34), 210 (91), 193 (22), 167 (22), 166 (25), 165 (BP); HR-MS (EI) Calcd. for $C_{15}H_{10}N_2O_2$: 254.1055; found: 254.1055.

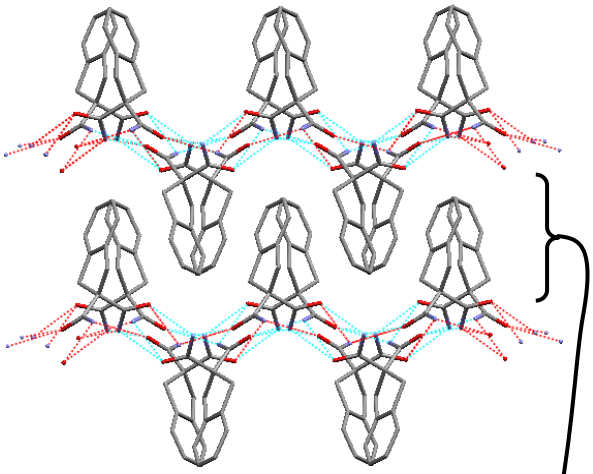
Crystal Structure of 1a

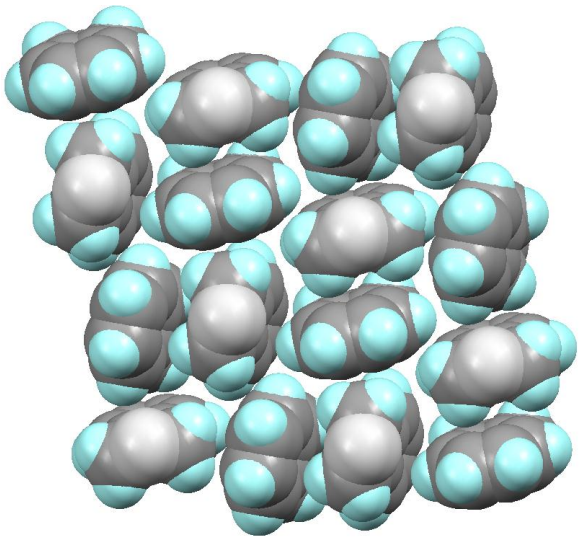


1a



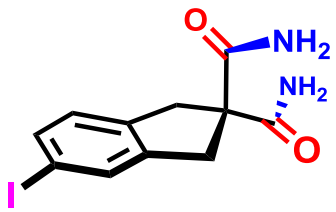




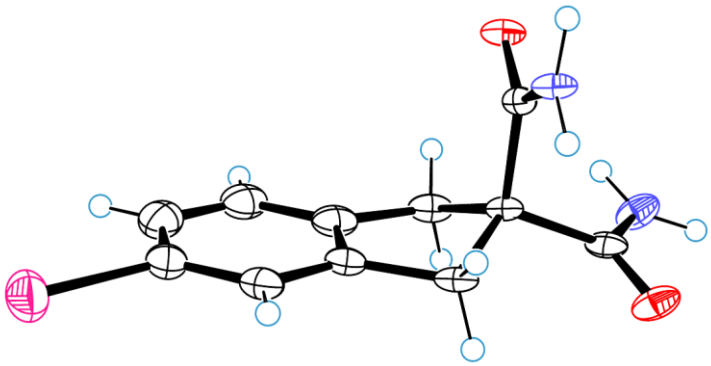


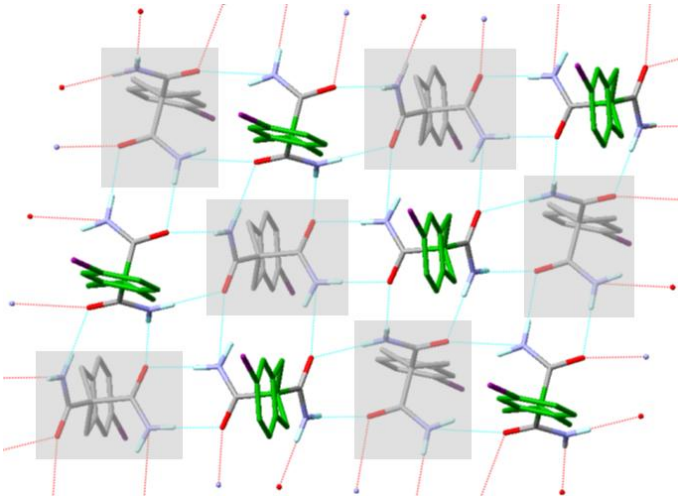
packing manner of indane units

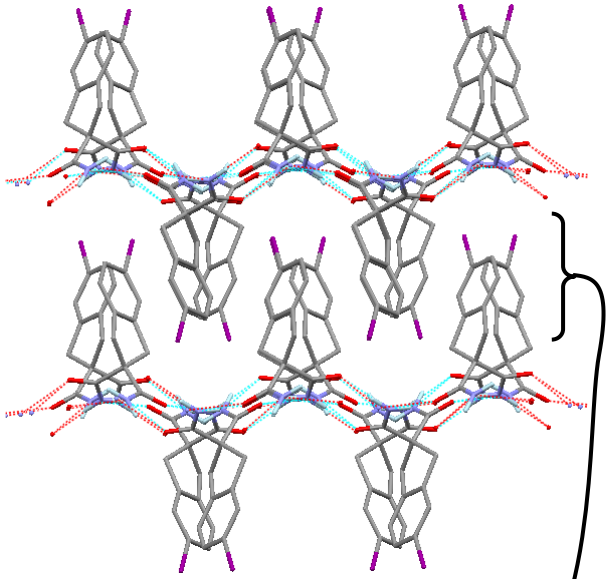
Crystal Structure of 1b

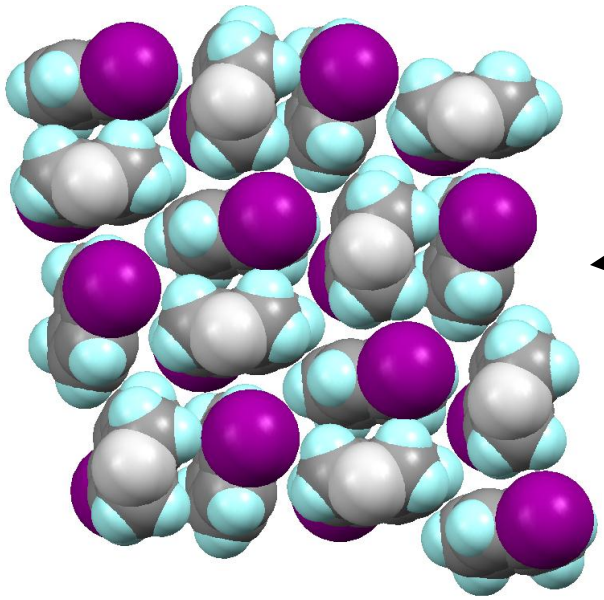


1b



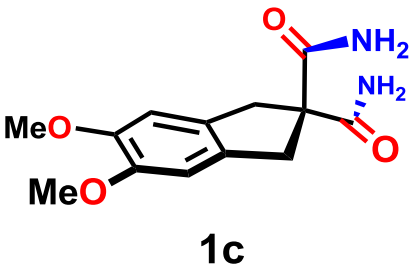




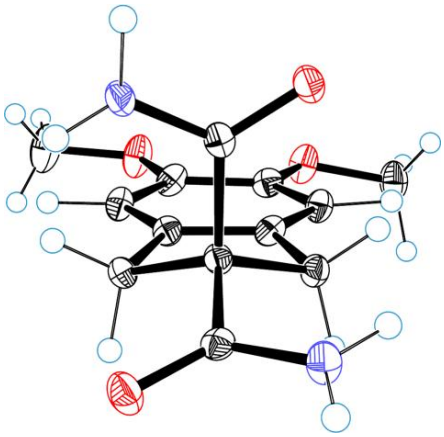


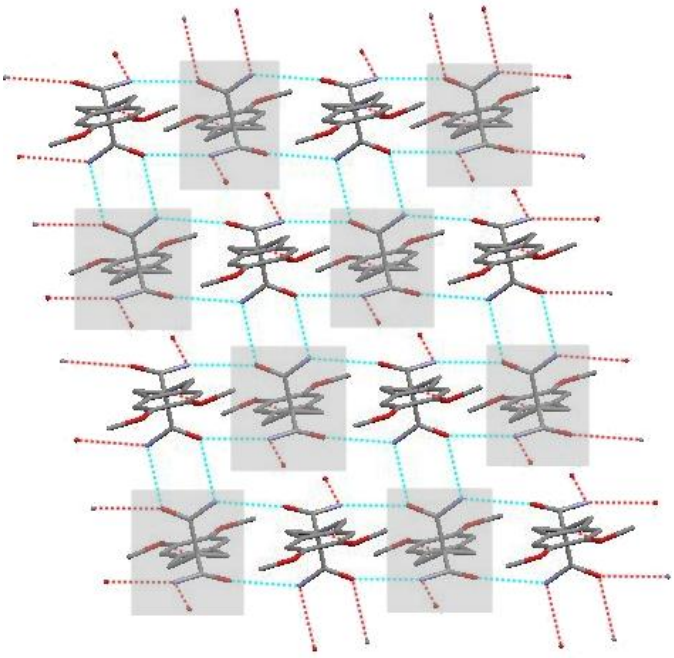
packing manner of indane units

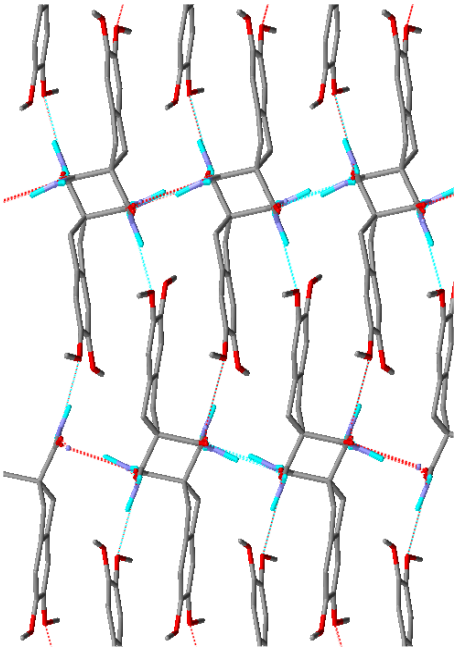
Crystal Structure of 1c

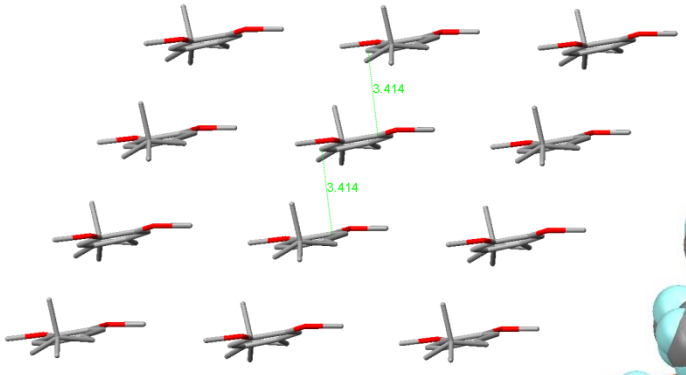


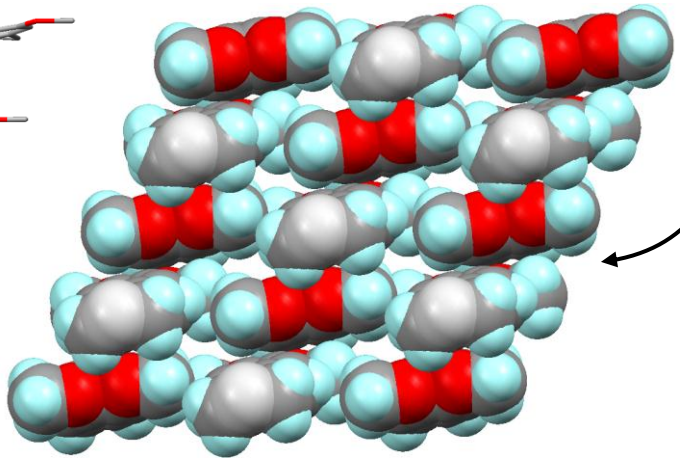
1c





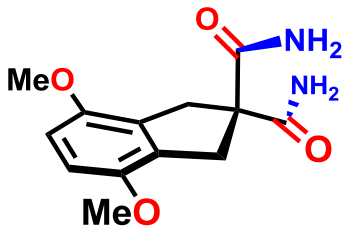




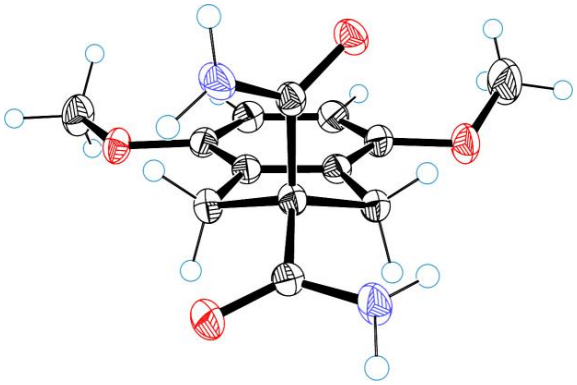


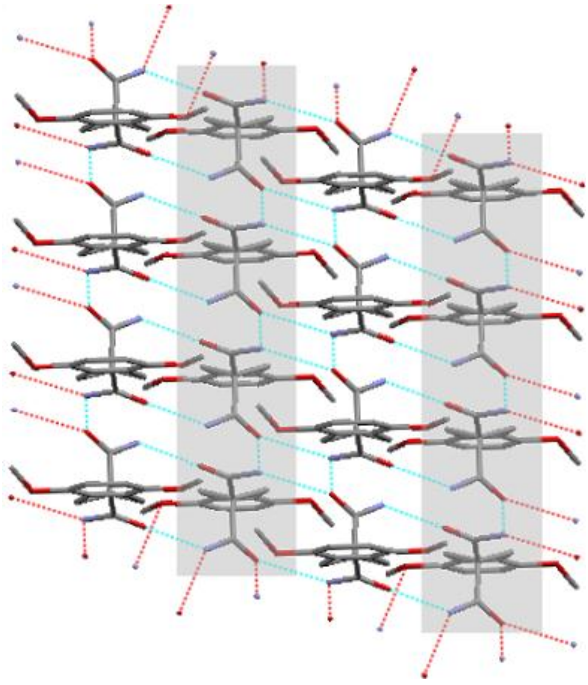
packing manner of indane units

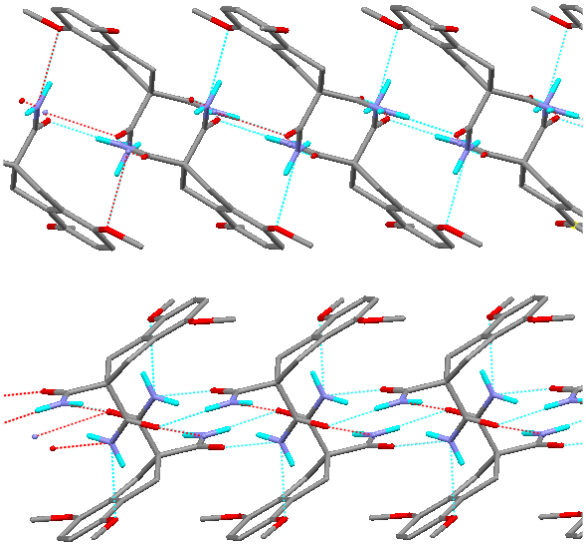
Crystal Structure of 1d

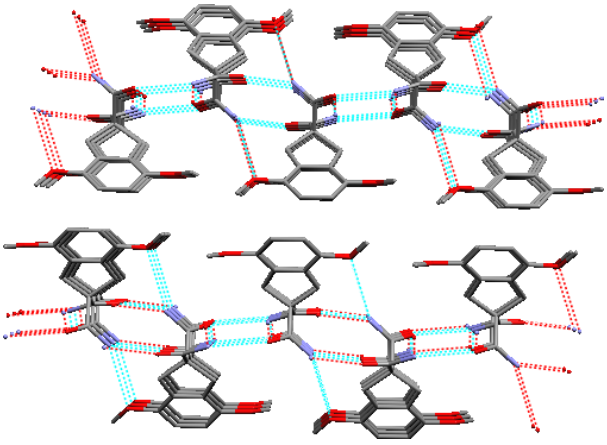


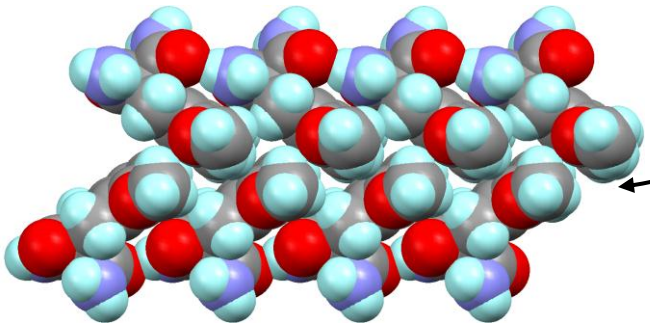
1d





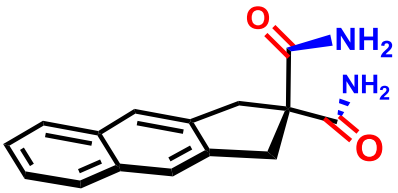




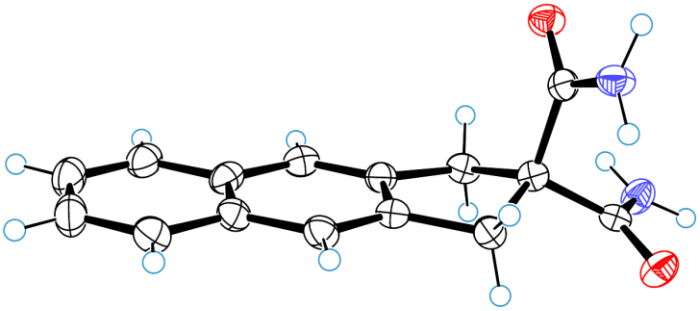


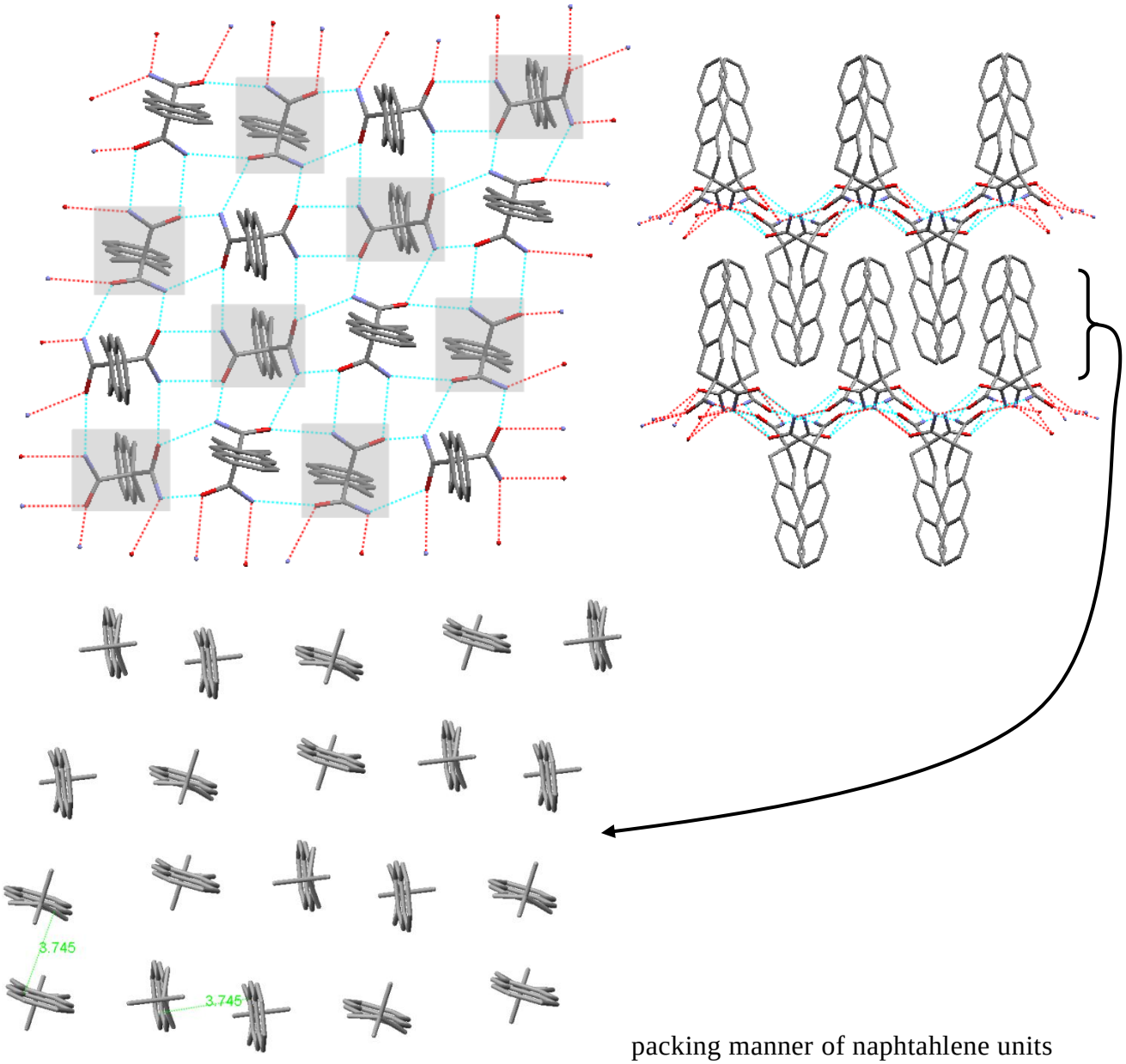
packing manner of indane units

Crystal Structure of 2a



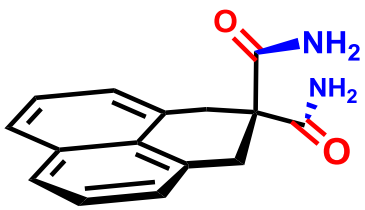
2a



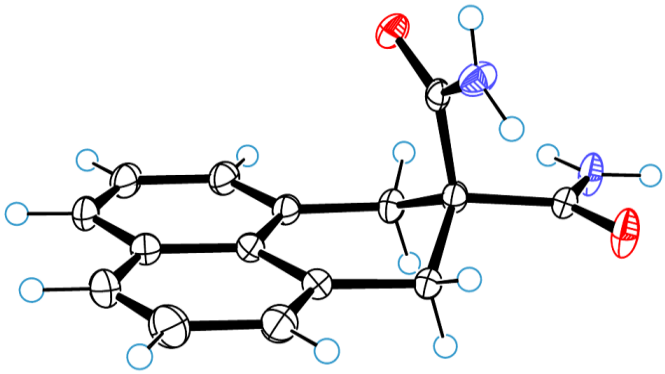


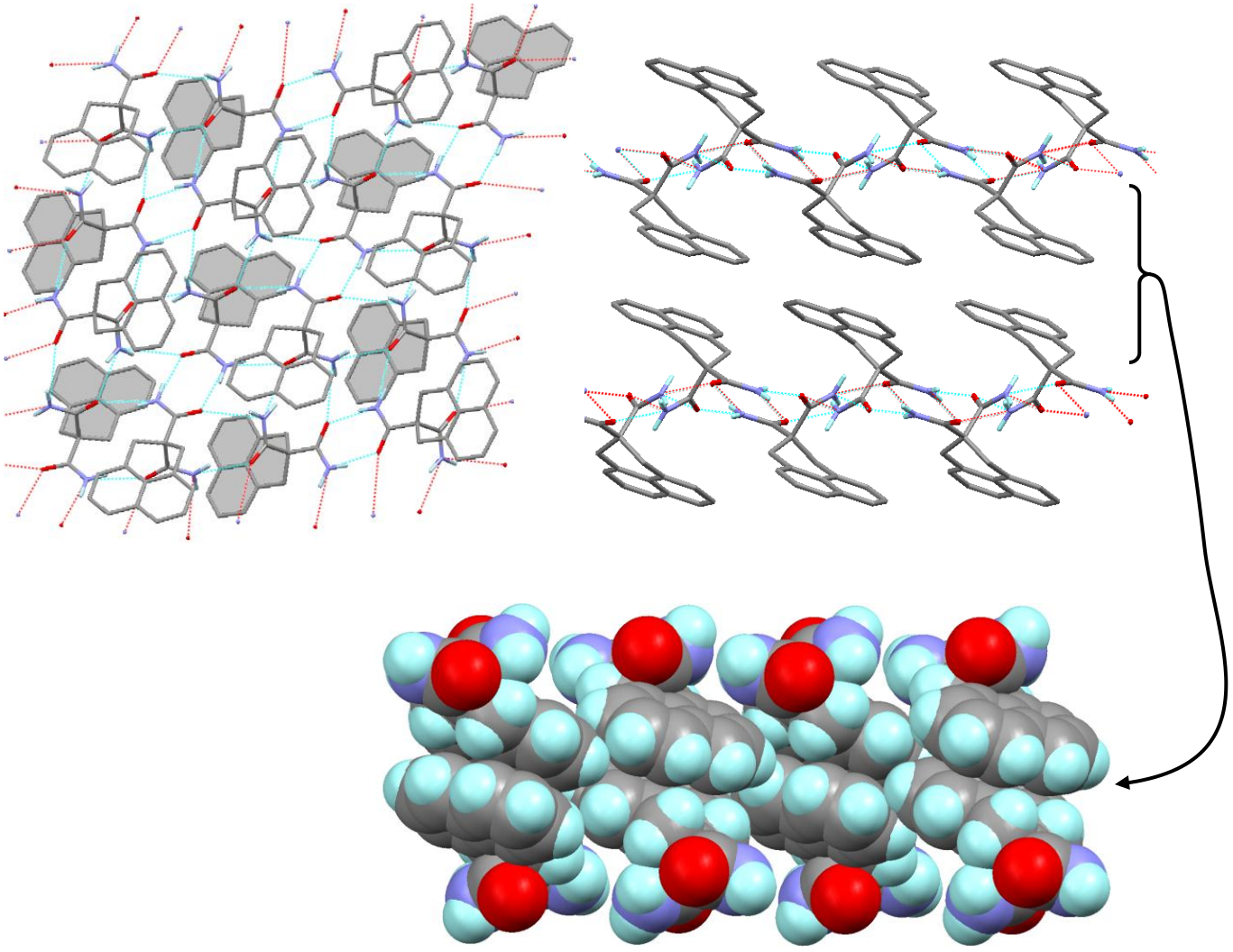
packing manner of naphtahlene units

Crystal Structure of 2b



2b





packing manner of naphtahlene units

Acknowledgement

We acknowledge the financial support from JSPS KAKENHI (No. 20750024) and JST PRESTO project. We gratefully acknowledges Prof. Takanori Suzuki and Prof. Kenshu Fujiwara (Hokkaido University) for kind disucussion. We thank Prof. Tamotsu Inabe (Hokkaido University) and Prof. Kazuo Miyamura (Tokyo University of Science) for the use of facilities to analyze the X-ray structures.

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