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## Introduction

Recently, the field of the construction of framework structures, such as metal–organic frameworks (MOFs),<sup>1–4</sup> covalent-organic frameworks (COFs),<sup>5–7</sup> or hydrogen-bonded organic frameworks (HOFs),<sup>8–10</sup> has been significantly developed. Various kinds of bonds and intermolecular interactions are used to construct these frameworks, and they can be carefully tailored by the researchers to yield frameworks for various functions. In this field, constructing a structure with two or more components is a powerful strategy to achieve a diversity of functionalized materials.

In addition to the relatively strong interactions, such as hydrogen bond coordination or ionic interactions, the weaker interactions can be exploited to yield a precise construction of the framework structures. The CH– $\pi$  or  $\pi$ – $\pi$  interaction (so-called aromatic–aromatic interactions), if it works alone, is weaker than the other interactions,<sup>11–13</sup> and there are not many examples of aromatic–aromatic interactions being used

# Co-crystals of 9,9'-bianthracene-10,10'dicarboxylic acid with linear bidentate basic ligand molecules: synthesis, crystal structure, and properties based on the layer structure exfoliated by water<sup>†</sup>

Misaki Okayasu, 🔟 Shoko Kikkawa, 🔟 Hidemasa Hikawa 🔟 and Isao Azumaya 🔟\*

Co-crystals of 9,9'-dianthracene-10,10'-dicarboxylic acid (1) with the linear bidentate bases 9,9'-biacridine (bac), phenazine (phez), 4,4'-dipyridine (dpy), and DABCO (dabco) were synthesized. In the crystal structures of the co-crystals of 1 and bac, phez, and dpy, one-dimensional (1D) structures were formed through the hydrogen bonding between the acid and the base. For each combination of the acid and the bases, several kinds of polymorphic co-crystals with a similar structure were obtained. Among them, a combination of 1 and dabco gave three kinds of co-crystals which had a layered structure. In one of the co-crystals, a phenomenon where layers of the crystals could be exfoliated by dropping water was observed. The two-dimensional (2D) fingerprinting plot of the co-crystals showed that the major interaction to form the 1D structure was O-H…N hydrogen bonding and that to form the layered structure was the CH– $\pi$  interaction, and the influence of the latter interaction on the robustness of the crystal was stronger than the former in the co-crystals.

as the main interactions when constructing a framework structure. However, aromatic–aromatic interactions work strongly when some parts of the molecules "fit" together. That is, when the molecules efficiently combine to fill some part of the space, this gives a stable crystal structure<sup>14,15</sup> even if each interaction is weak. Thus, using the CH– $\pi/\pi$ – $\pi$  interaction by adding a broad aromatic ring can be a common strategy to design crystal structures, even if it is not the main interaction.<sup>16–20</sup> In line with this strategy, we have previously reported functional crystals in which one-dimensional (1D) structures are self-assembled using a coordination linkage and CH– $\pi/\pi$ – $\pi$  interactions.<sup>21</sup>

Various interactions are also exploited in the design of a co-crystal. If two or more compounds are used in constructing crystalline materials, the obtained crystals are called co-crystals.<sup>22–25</sup> Co-crystals have been studied especially in the pharmaceutical field because co-crystals with different coformers will naturally exhibit different properties, such as stability, solubility, and bioavailability.<sup>26–28</sup> From the viewpoint of materials science, the phenomenon of co-crystallization has shown great potential for providing a wide variety of crystalline materials by a combination of two or more compounds which will mutually interact.

To design co-crystals, the three-dimensional (3D) shape of each component is also important in addition to the intermolecular interactions. That is, the concepts of the

Faculty of Pharmaceutical Sciences, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan. E-mail: isao.azumaya@phar.toho-u.ac.jp; Fax: +81 47 472 1585: Tel: +81 47 472 1589

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molecular synthon and embrace are important in crystal engineering, which are based on intermolecular interactions of the 3D shapes of the molecule. These concepts have enabled the design of various crystal structures, like retrosynthesis in synthetic chemistry.<sup>29</sup>

Based on these concepts, we have synthesized a novel building block that can interact with neighboring molecules by two types of interactions (Scheme 1). Dicarboxylic acid 1 has carboxy groups that can form hydrogen bonding (acidbase interactions), and anthracene rings that have the potential to form  $CH-\pi/\pi-\pi$  interactions. Therefore, compound 1 is versatile as a building block for designing functional crystalline materials including co-crystals.

In this study, we synthesized compound **1** and its various co-crystals with linear bidentate basic ligand molecules (Fig. 1), 9,9'-biacridine (**bac**), phenazine (**phez**), 4,4'-dipyridine (**dpy**), and DABCO (**dabco**), using several types of weak intermolecular interactions, mainly hydrogen bonds (acid-base interactions) and CH– $\pi/\pi$ – $\pi$  interactions. In the co-crystals of **1** and the base molecules, molecule **1** and the base molecule generally aligned alternately through O–H…N acid-base interactions (hydrogen bonds) to form a 1D structure, and the bianthracene moieties were assembled by CH– $\pi$  interactions, which worked perpendicularly between the aromatic rings to form a 2D sheet.

## Experimental

#### Materials

Anthraquinone was purchased from TCI Co., Ltd., Tokyo, Japan. Zinc powder was purchased from KANTO Chemical Co., Inc., Tokyo, Japan. *n*-BuLi, bromine, and solvents (ethyl acetate, tetrahydrofuran, HCl, acetic acid, 1,2-dichloroethane, and methanol) were purchased from FUJIFILM Wako Pure Chemical Corporation. All commercially available reagents and solvents were used without further purification.

#### Analytical techniques

Fourier transform infrared spectroscopy (FT-IR) was performed on a JASCO FT/IR-4100 spectrometer using KBr tablets. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) and carbon-13 NMR (<sup>13</sup>C-NMR) spectra were recorded on a JEOL JNM-ECS400 (400 MHz) spectrometer. Chemical shifts ( $\delta$ ) are



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relative to tetramethylsilane (TMS) (0 ppm) in  $CDCl_3$  and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, dd = double doublet, ddd = double double doublet. Mass spectroscopy (MS) and high resolution mass spectroscopy (HRMS) were performed on a JEOL JMS-AM SYSTEM II-50.

#### Single crystal X-ray diffraction analysis

Single crystals were mounted on loop for the X-ray measurements. Diffraction data were collected on an X-ray diffractometer (Rigaku XtaLAB P200) equipped with a rotating anode X-ray source (Mo-K $\alpha$ ,  $\lambda = 0.71075$  Å: 1dpy, **1dabco-b**, **1dabco-c**, Cu-K $\alpha$ ,  $\lambda$  = 1.54187: **1**, **1bac**, **1phez**, 1dabco-a) and a hybrid photon counting detector (PILATUS 200 K) at 93 K. The frame data were integrated, and the absorption correction was calculated using the Rigaku CrystalClear, CrysAlisPro program package. The structures were solved by direct methods or Patterson methods (SHELXT Version 2014/5 (ref. 30)), and refined by full-matrix least-squares fitting on  $F^2$  (SHELXL2013, SHELXL Version 2014/7, 2018/3). All non-hydrogen atoms were refined anisotropically and hydrogen atoms were theoretically added. The crystal data and the structure refinements are summarized in Table 1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 1952757-1952763.

#### Synthesis of 9,9'-bianthracene<sup>31,32</sup>

Anthraquinone (25.03 g, 0.12 mol) was dissolved in acetic acid (600 mL). Zinc powder (55.06 g, 0.84 mol) was added to the solution under stirring using a mechanical stirrer, and the reaction mixture was heated to 90 °C. Concentrated HCl





Table 1 Crystallographic data and details of diffraction experiments for the co-crystals

Cocrystal	1	1bac	1phez	1dpy	1dabco-a	1dabco-b	1dabco-c
Formula	C80H78O14	C <sub>28</sub> H <sub>17</sub> NO <sub>2</sub>	$C_{42}H_{26}N_2O_4$	C40H26N2O4	C44.8H39.6N3.6O8.2	$C_{42}H_{42}N_4O_{11}$	C42H43N4O11
Formula weight	1263.49	399.45	622.68	598.66	759.62	778.81	779.82
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	Pbcn	Pbca	$P2_1/c$	$P\bar{1}$	Сс	$Pna2_1$
a/Å	9.18848(15)	11.97202(19)	12.1391(2)	14.3335(5)	10.3818(5)	10.2344(8)	33.4734(10)
b/Å	18.3718(2)	12.27700(18)	12.75610(12)	11.8876(4)	10.9676(2)	33.477(2)	10.5712(4)
c/Å	19.60910(18)	12.64035(17)	38.9751(4)	16.9672(6)	18.7727(5)	11.5077(10)	11.1961(4)
a/o	98.7879(9)	90	90	90	95.299(2)	90	90
β/°	92.6442(10)	90	90	96.463(3)	98.714(3)	93.536(7)	90
$\gamma/^{\circ}$	97.7172(13)	90	90	90	91.279(3)	90	90
$V/\text{\AA}^3$	3234.19(7)	1857.88(5)	6035.20(13)	2872.64(17)	2102.39(12)	3935.2(5)	3961.8(2)
Z	2	4	8	4	2	4	4
T/K	93	93	93	93	93	93	93
$\mu/\mathrm{mm}^{-1}$	0.713	0.713	0.711	0.090	0.70	0.096	0.095
<sup><i>a</i></sup> GOF on $F^2$	1.029	1.050	1.146	1.024	1.593	0.995	1.04
Reflections collected	43 3 57	21 955	79 408	45 664	55 3 4 7	31178	32 412
Independent reflections $I > 2\sigma(I)$	10419	1537	4986	4351	4608	4291	5920
Restraints/parameters	0/859	0/166	0/441	0/423	64/585	2/517	1/521
R <sub>int</sub>	0.0269	0.0349	0.0593	0.0822	0.1150	0.1157	0.0596
${}^{b}R_{1}$ [on F, $I > 2\sigma(I)$ ]	0.0802	0.0453	0.0954	0.053	0.1379	0.1064	0.0560
$^{c}$ w $R_{2}$ (on $F^{2}$ , all data)	0.2417	0.1307	0.2908	0.1176	0.4352	0.2994	0.1536
Largest diff. peak/hole/e Å <sup>-3</sup>	0.62/-0.56	0.26/-0.36	0.59/-0.36	0.26/-0.30	1.29 / -0.41	0.55 / -0.37	0.42/-0.35
CCDC no.	1952757	1952758	1952759	1952760	1952761	1952762	1952763
<sup><i>a</i></sup> GOF = $[\sum w(F_0^2 - F_c^2)^2 / (N_0 - N_v)]^{1/2}$ ( $N_0$ ; number of observations, $N_v$ ; number of variables). <sup><i>b</i></sup> $R_1 = \sum   F_0  -  F_c   / \sum  F_0 $ . <sup><i>c</i></sup> $wR_2 = [\sum (w(F_0^2 - F_0^2)^2 / (N_0 - N_v)]^{1/2}$							

 $F_{\rm c}^{2})^{2})/\sum w(F_{\rm o}^{2})^{2}]^{1/2}$ 

(150 mL) was dropped into the solution using a dropping funnel over 30 min. The mixture was kept at 90 °C for 2 h under stirring. After cooling to room temperature, the reaction mixture was added to water (50 mL) under ice cooling. The solid was collected by filtration and washed with water. The solid was dissolved in toluene (500 mL), and heated to 120 °C under reflux. The solution was filtered whilst hot, and the filtrate was allowed to stand overnight. 9,9'-Bianthracene was obtained as yellow crystals (22.37 g, 52% yield). <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$  8.68 (s, 2H), 8.15 (d, *J* = 8.6, 4H), 7.44 (ddd, *J* = 8.3, 6.6, 1.2, 4H), 7.14 (ddd, *J* = 8.8, 6.3, 1.2, 4H), 7.08 (dd, *J* = 8.8, 1.26, 4H).

#### Synthesis of 10,10'-dibromo-9,9'-bianthracene<sup>31,32</sup>

9,9'-Bianthracene (3.50 g, 9.87 mmol) was dissolved in 1,2dichloroethane (70 mL). Bromine (1.1 mL, 2 eq.) was slowly dropped into the solution, and the reaction mixture was stirred for 3 h. After cooling in an ice bath, the yellow solid was collected by vacuum filtration, and washed with 1,2dichloroethane (3.66 g, 73% yield). <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$  8.69 (ddd, J = 9.4, 0.9, 0.4, 4H), 7.58 (ddd, J = 9.0, 6.4, 1.2, 4H), 7.18 (ddd, J = 9.0, 6.4, 1.2, 4H), 7.07 (ddd, J = 8.8, 0.8, 0.4, 4H).

#### Synthesis of 9,9'-dianthracene-10,10'-dicarboxylic acid (1)

10,10'-Dibromo-9,9'-bianthracene (81.16 mg, 0.16 mmol) was dissolved in anhydrous diethyl ether (3 mL). The mixture was stirred for 15 min at -15 °C under an atmosphere of argon. *n*-BuLi (0.3 mL, 1.6 M) was added dropwise, and then the mixture was stirred for 1.5 h. CO<sub>2</sub> was bubbled into the

reaction mixture for 30 min at room temperature. 0.2%  $K_2CO_3$  (10 mL) was added under stirring for 2 h, and the mixture was neutralized with concentrated HCl. The white solid was collected by vacuum filtration and washed with water (49.73 mg, 71% yield). The crystals were crystallized from tetrahydrofuran. M.p. > 295 °C (dec.). FT-IR (KBr, cm<sup>-1</sup>): 3382, 1684, 1561, 1488, 1441, 1392, 1320, 1290, 1247, 1026, 860, 770, 679, 599, 472. <sup>1</sup>H NMR (400 MHz, 313 K, DMSO-*d*<sub>6</sub>):  $\delta$  8.24 (d, *J* = 8.7, 4H), 7.48 (t, *J* = 7.3, 7.8, 4H) 7.18 (t, *J* = 8.7, 6.4, 4H), 6.91 (d, *J* = 8.7, 4H); <sup>13</sup>C NMR (100 MHz, 313 K, DMSO-*d*<sub>6</sub>): 170.5, 130.5, 130.5, 126.7, 126.1, 126.0, 125.9, 125.5. HRMS (EI, *m/z*) calcd. for C<sub>30</sub>H<sub>18</sub>O<sub>4</sub> [M<sup>+</sup>] = 442.1200. Found 442.1205. Anal. calcd. for C<sub>30</sub>H<sub>25</sub>O<sub>7.5</sub> = C<sub>30</sub>H<sub>18</sub>O<sub>4</sub>·(H<sub>2</sub>O)<sub>3.25</sub>: C, 71.93; H, 4.9; N, 0.00%. Found: C, 71.64; H, 4.52; N, 0.00%.

#### Crystallization

Co-crystals of **1** with linear bidentate bases, **bac**, **phez**, **dpy**, and **dabco**, were synthesized by liquid/liquid diffusion or grinding. Three co-crystals of **1** and **dabco** were obtained: **1dabco-a**, **1dabco-b** and **1dabco-c**.

**1bac.** Solutions of compound **1** (16.9 mg,  $3.8 \times 10^{-5}$  mol) in tetrahydrofuran (7 mL) and **bac** (5.0 mg,  $1.4 \times 10^{-5}$  mol) in acetonitrile (3 mL) were prepared. The solution of compound **1** was dispensed into five glass vessels (200 µL per vessel), then the solution of bac (200 µL) was layered onto each solution of compound **1**. After the solution at room temperature (rt) was left for **1** week, yellow crystals were obtained.

**1phez.** Solutions of compound **1** (4.4 mg,  $9.9 \times 10^{-6}$  mol) in ethyl acetate (2 mL) and **phez** (1.9 mg,  $1.0 \times 10^{-5}$  mol) in

*n*-hexane (2 mL) were prepared. The solution of compound **1** was dispensed into eight glass vessels (200  $\mu$ L per vessel), and then the solution of **phez** (200  $\mu$ L) was layered onto each solution of compound **1**. After the solution at rt was left for 3 days, yellow crystals were obtained.

**1dpy.** Compound **1** (2.4 mg,  $5.4 \times 10^{-6}$  mol) and **dpy** (2.2 mg,  $1.4 \times 10^{-5}$  mol) were ground using an agate mortar. A solution of the mixture in methanol (600 µL) was prepared. The solution of compound **1** and **dpy** was dispensed into three glass vessels (200 µL per vessel). After the solution at rt was left for 5 days, red crystals were obtained.

**1dabco-a.** Solutions of compound **1** (2.8 mg,  $6.3 \times 10^{-6}$  mol) in ethyl acetate (2 mL) and **dabco** (4.2 mg,  $3.7 \times 10^{-5}$  mol) in tetrahydrofuran (2 mL) were prepared. The solution of compound **1** was dispensed into eight glass vessels (200 µL per vessel), then methanol (100 µL) and the solution of **dabco** (200 µL) were layered onto each solution of compound **1**. After the solution at rt was left for 1 week, red crystals were obtained.

**1dabco-b.** Solutions of compound **1** (1.2 mg,  $2.7 \times 10^{-6}$  mol) in ethyl acetate (6 mL) and **dabco** (2.4 mg,  $2.1 \times 10^{-5}$  mol) in tetrahydrofuran (6 mL) were prepared. The solution of compound **1** was dispensed into 24 glass vessels (200 µL) per one vessel), and then the solution of **dabco** (200 µL) was layered onto each solution of compound **1**. After the solution at rt was left for 1 week, red crystals were obtained.

**1dabco-c.** Solutions of compound **1** (0.8 mg,  $1.8 \times 10^{-6}$  mol) in tetrahydrofuran (10 mL) and **dabco** (1.2 mg,  $1.1 \times 10^{-5}$  mol) in ethyl acetate (2 mL) were prepared. The solution of compound **1** was dispensed into eight glass vessels (200  $\mu$ L per vessel), and then the solution of **dabco** (200  $\mu$ L) was layered onto each solution of compound **1**. After the solution at rt was left for 1 week, red crystals were obtained.

## Results and discussion

Crystal structures of the co-crystals were determined by single crystal X-ray diffraction (SXRD) analysis. 2D fingerprint plots as Hirshfeld surfaces were calculated using Crystal Explorer 17.5.<sup>33–35</sup>

#### Crystal structure of 1

A crystal of compound **1** was obtained from tetrahydrofuranwater by vapor diffusion (Fig. 2). The crystal structure in the  $P\bar{1}$  space group had two molecules of **1**, five tetrahydrofuran molecules, and one H<sub>2</sub>O molecule in the asymmetric unit. The torsion angles of C10–C11–C16–C17, C10–C11–C16–C29, C40–C41–C46–C59, and C40–C41–C46–C47 were +94.74°, ~88.50°, +87.38°, and ~93.10°. No CH– $\pi$  or  $\pi$ – $\pi$  interactions were observed between bianthracene moieties of the neighboring molecules.

# 1D structures and their assemblies in co-crystals: 1bac, 1phez and 1dpy

All three co-crystals formed 1D coordination polymers. **1** and the base molecule aligned alternately through acid-base



**Fig. 2** Crystal structure of **1**: (a) view along the *a*-axis, (b) *b*-axis, and (c) *c*-axis. Colors: C, gray; O, red. The aromatic H atoms are omitted for clarity.

interactions formed a straight 1D structure where the molar ratio of 1 and the base molecule was 1:1. In all these cocrystals, the 1D structures are constructed with hydrogen bonds that are further assembled into extended structures by CH- $\pi$  and  $\pi$ - $\pi$  interactions.

In co-crystal **1bac** (Fig. 3), molecules **1** and **bac** were disordered at the same position and the positions of each atom of COOH…N were the same because they had very similar molecular shapes. Regardless, it was proposed that they should align alternately judging from the demand of their chemical structure. Additionally, co-crystal **1bac** crystallized in the orthorhombic system and space group *Pbcn*. The distance and angle of the joint part in the



**Fig. 3** Crystal structure of **1bac**: (a) 1D structure consisting of **1** and **bac**, (b) view from the top of 1D structures, and (c) view from the side of 1D structures. Colors: C, gray; N, violet; O, red. The aromatic H atoms and disordered atoms are omitted for clarity.

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structure (O1-H1…N1) were 2.665 Å and 170.96°. The C10-C11-C11-C12 torsion angles were +71.31° and -107.56°.

Co-crystal **1phez** crystallized in the orthorhombic system and space group *Pbca* (Fig. 4). The asymmetric unit consisted of one molecule of **1** and one molecule of **phez**. Molecule **1** and **phez** formed 1D chains through acid–base interactions, which were aligned parallel to the *c*-axis. The distance and angle between atoms associated with hydrogen bonding were as follows: O1–H1…N1 (2.710 Å, 176.73°) and O3–H3…N2 (2.708 Å, 174.96°). The void space of the cocrystal was 247.7 Å in the unit cell, which corresponded to 4.1%. The torsion angles of C10–C11–C16–C17 and C10–C11–C16–C29 were +72.21° and –108.95°.

Co-crystal **1dpy** crystallized in the monoclinic system and space group  $P2_1/c$  (Fig. 5). The asymmetric unit consisted of one **1** and one **dpy**. The torsion angles of C10–C11–C16–C17, C10–C11–C16–C29, C32–C33–C38–C37, and C32–C33–C36–C37 were –81.35°, 102.13°, 44.75°, and –136.42°. The distances and angles of the joint part in the structure were 2.605 Å and 169.37° (O1–H1…N1), and 2.612 Å and 174.69° (O3–H3…N2).

Co-crystals **1dabco-a**, **1dabco-b**, and **1dabco-c** grew as crystals with a thin square shape and were composed of **1**, **dabco**, and a different number of  $H_2O$  molecules. Very similar layer structures were formed in these co-crystals, which consisted of molecules of **1** and **dabco**. The molecules of **1** in the layer structure assembled perpendicular to the direction of the bianthracenyl axis by the CH- $\pi$  and  $\pi$ - $\pi$  interaction of the anthracene skeletons. This layer is referred to as a bianthracene layer. In co-crystals **1dabco-a-c**, **dabco** molecules filled the void between the bianthracene layers. Lattice parameters were very similar in these cocrystals. The



**Fig. 4** Crystal structure of **1phez**: (a) 1D structure consisting of **1** and **phez**, (b) view from the top of 1D structures, (c) view from the side of 1D structures. Colors: C, gray; N, violet; O, red. The aromatic H atoms are omitted for clarity.



**Fig. 5** Crystal structure of **1dpy**: (a) 1D structure consisting of **1** and **dpy**, (b) view from the top of the 1D structures, and (c) view from the side of the 1D structures. Colors: C, gray; N, violet; O, red. The aromatic H atoms are omitted for clarity.

difference among these co-crystals was based on the number of water molecules contained and the way the bianthracene layers were stacked. The bianthracene layers were connected by O-H...N hydrogen bonding of 1, dabco, and H<sub>2</sub>O molecules. Judging from the atom distance concerning the acidic proton, a proton transfer between 1 and dabco occurred. This is supported by the fact that if a  $\Delta p K_a$  value between a protonated and an acid base is more than 4, both of them tend to exist in ionic forms<sup>36</sup> and that the  $pK_a$  of and anthracene-9-carboxylic protonated dabco acid (corresponding to a partial structure of 1) are 8.82 (ref. 37) and 3.77.38 Since there were dabco and a lot of H<sub>2</sub>O molecules between the layers, these piles of bianthracene layers were physically soft and fragile.

The structures and differences of 1dabco-a, 1dabco-b, and 1dabco-c were as follows. Crystal 1dabco-a crystallized in the triclinic system and space group  $P\overline{1}$  (Fig. 6(a)). The asymmetric unit consisted of one molecule of 1, two dabco, one ethyl acetate, and three H<sub>2</sub>O molecules. The disorders observed in 1dabco-a were complicated because the water molecule was also involved in the disorders. The dabco molecule was partly replaced with H<sub>2</sub>O (only one molecule could be assigned because of its low occupancy), and the best result for structural optimization was obtained when the occupancy rates were 0.8 (dabco) and 0.2 (H<sub>2</sub>O). The ethyl acetate molecule was differently ordered corresponding to whether the neighbouring molecule would be **dabco** or H<sub>2</sub>O. The layered structures were stacked along the c-axis. The thickness of the layer was 12.5 Å, and the distance between layers was 6.1 Å. In the crystal structure of **1dabco-a**, not only the layer structures but also a chained 1D structure were observed. The 1D structure included one molecule of 1 and



Fig. 6 Crystal structure of (a) 1dabco-a, (b) 1dabco-b, (c) 1dabco-c. Description of the stacking pattern of the bianthracene layer.

one **dabco** molecule, while the other **dabco** molecules existed as guest molecules with ethyl acetate between the 1D chains. The guest **dabco** molecules and ethyl acetate molecules were disordered. The 1D chains were aligned parallel to the *c*-axis. The distances and angles of atoms involved in hydrogen bonding were 2.527 Å and  $153.4^{\circ}(O1\cdots H1A\cdots N1)$ , 2.566 Å and  $169.61^{\circ}$  ( $O3\cdots H3A\cdots N2$ ). The torsion angles of C10–C11–C16– C29 and C10–C11–C16–C17 were +85.85° and -93.15°.

**1dabco-b** crystallized in the monoclinic system and space group C2/c (Fig. 6(b)). The layered structures were stacked along the *b*-axis. The neighboring upper and lower layers in **1dabco-b** staggered to the *a*-axis direction. The thickness of the layer was 11.8 Å, and the distance between layers was 5.0 Å. The distance and angle of O1…H1A…N1 were 2.645 Å and 152.24°. The torsion angles of C10–C11–C16–C29 and C10– C11–C16–C17 were +82.81° and –92.21°.

**1dabco-c** crystallized in the orthorhombic system and space group  $Pna2_1$  (Fig. 6(c)). The layered structures were stacked along the *a*-axis. The layers of **1dabco-c** were inverted, rotated by 180° and slid in the *a* and *c*-axis directions. Moreover, the thickness of the layer was 12.0 Å, the distance between layers was 4.7 Å. The distance and angle of O2…H1…N1 were 2.748 Å and 157.82°. The torsion angles of C10–C11–C16–C29 and C10–C11–C16–C17 were +88.19° and –88.15°.

Next, the face indices were calculated from the structural analysis and were assigned to the crystal appearance. The wide surface (100) matched with the horizontal surface of the layer (Fig. 7). **1dabco-a**, **1dabco-b**, and **1dabco-c** grew with a thin square shape. Although the square shape became large as the crystal grew, the crystal did not become thick.

#### Two dimensional fingerprint plot analysis

The intermolecular interactions in these co-crystals were analyzed using Hirshfeld surface analyses (Fig. 8). The relative contributions by hydrogen bonds and those by  $CH-\pi$ interactions were determined. The contribution of hydrogen bonds was shown as the sum of H…N contacts and O…H contacts taking into account that a proton transfer could occur between **1** and **dabco** (the second line of the small square figures in Fig. 8(a)). Also, the contribution of  $CH-\pi$ interactions was shown as the sum of H…C contacts and C…H contacts (third line of the small square figure in Fig. 8(a)). Among the  $CH-\pi$  interactions, the H…C contacts show the T-shape  $CH-\pi$  interaction<sup>11-13</sup> between anthracene rings and the C…H contact shows the  $CH-\pi$  interaction between the anthracene ring and guest **dabco**. First, the contribution of the hydrogen bond appeared in **1phez** 



Fig. 7 Crystal face and crystal appearance.



Fig. 8 (a) 2D fingerprint plots for **1phez**, **1dpy**, **1dabco-a**, **1dabco-b**, and **1dabco-c**, (b) percentage contributions to the Hirshfeld surface area of the intermolecular contacts in the crystal structures of **1phez**, **1dpy**, **1dabco-a**, **1dabco-b**, and **1dabco-c**, (c) positions and directions of intermolecular contacts.

(17.3%), 1dpy (16.4%), and 1dabco-a (15.6%) judging from the shape of the Hirshfeld surface and the ratio of their contribution, which meant that 1D chained structures were constructed in the crystals. The ratios were larger than those of 1dabco-b (11.9%) and 1dabco-c (11.9%) that have layered structures. Next, a contribution of CH- $\pi$  interaction contacts significantly appeared in 1dabco-a, 1dabco-b, and 1dabco-c (40.2, 33.7, and 34.1%) because the Hirshfeld surface was spread broadly centered around distances of 1.2/1.8  $(d_e/d_i)$  Å and the ratios of their contributions were much larger than those of 1phez (31.4%) and 1dpy (24.6%). That is, to maintain the crystal framework, the contribution of the sum of CH- $\pi$  interactions between anthracene moieties and those between the anthracene moiety and guest dabco was larger than the sum of the hydrogen bonding interactions, in the order 1dabco-a < 1dabco-b < 1dabco-c.

#### Exfoliation of the layer structure by water

We tried to determine the characteristic of the layer structure of the co-crystals. When the co-crystal of **1dabco-c** was exposed to water, a phenomenon where the layers of the cocrystal were immediately exfoliated was observed. The exfoliation method is shown in Fig. 9 and a video presentation is provided in the ESI.<sup>†</sup> The layers were not exfoliated using other usual solvents such as methanol, chloroform, *n*-hexane, or tetrahydrofuran. Similar phenomena were observed in **1dabco-a** and **1dabco-b**. When we dropped water on the crystals of **1bac**, **1phez** and **1dpy**, they remained unchanged. Although the details of the exfoliation mechanism remain unclear, water molecules between the layer of **1** may be relatively movable and allow penetration of added water molecules through the gap between the layers. All the exposed carboxyl groups can then bond with water molecules through hydrogen bonding, and the surface of the layer may become coated with water molecules. However, because the inside of the layer consists of aromatic rings (lipophilic site) through the CH– $\pi$  or  $\pi$ – $\pi$  interactions, the layers may be robust against water (Fig. 10). The hydrogen bonded **dabco** molecules bind the layers of



Fig. 9 Microscopy visualization of the time-dependent change in the single crystals of **1dabco-c** for 13 seconds after dropping water.



Fig. 10 Proposed mechanism of exfoliation of the layer structure.

molecules of **1** in cocrystals **1dabco-a-c** through hydrogen bonding, then the **dabco** molecules flow out from between the layers with the layers being exfoliated by soaking in water. Meanwhile, the guest **dabco** molecules are snugly captured in the layers of **1** through  $CH-\pi$  interactions, and then they remain longer in the layers when soaked in water. Thus, these two kinds of **dabco** molecules are thought to act in a different way when the cocrystals are soaked in water, although it is difficult to prove because they cannot be distinguished. This mechanism correlated with the results suggested by the 2D fingerprint plots that the  $CH-\pi$  interaction influenced the crystal robustness more strongly than the hydrogen bonding (N···HO) in **1dabco-a-c**.

## Conclusions

In summary, we synthesized a novel compound 1 that was co-crystallized with linear bidentate bases. The co-crystals of compound 1 and bac, phez, and dpy had 1D structures and the three co-crystals of compound 1 and dabco had layered structures. It was possible to distinguish these layered cocrystals by the way that the layers overlapped. In addition, cocrystal **1dabco-c** included H<sub>2</sub>O molecules between the layers, so the layers were exfoliated when the co-crystal was soaked in water. Meanwhile, 2D fingerprint plots provided a deeper understanding of the contribution of intermolecular interactions in the cocrystals. When the hydrogen bond (N···HO) was relatively strong, a 1D structure was formed primarily, and when the CH- $\pi$  interaction was relatively strong, a layered structure was formed primarily. The present results not only provide insight into the novel building block, but also open new avenues for manipulating weak intermolecular interactions and the design of a co-crystal consisting of two or more molecules.

# Conflicts of interest

There are no conflicts to declare.

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