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Generation of Zwitterionic Water Channels: Biszwitterionic Imidazolium Carboxylates as Hydrogen-Bonding Acceptors

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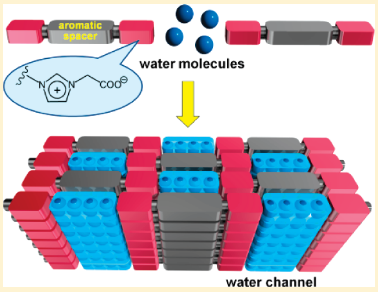
Supporting Information

ABSTRACT: Organic crystals containing several types of water channels are generated by clipping water molecules with biszwitterionic imidazolium carboxylates as hydrogen-bonding acceptors. The types of water channels to be generated depend on the size and the shape of the aromatic spacers tethered with two imidazolium carboxylates moieties. Clusters of water tetramers and dimers were obtained from imidazolium carboxylates with phenylene (**1**) and naphthalene (**2**) linkers, respectively. The latter showed pseudopolymorphism, affording layers of water hexamers. Imidazolium carboxylate possessing biphenylene linker (**3**) afforded channels of discrete water tetramers.



Considerable effort has been devoted to design water clusters in recent years. Investigations of small water clusters from both experimental and theoretical points of view have been performed to understand the structure and nature of bulk water,[1] which are entirely dependent on H-bonding interactions and fluctuations among water molecules. They are of fundamental importance in biological, chemical, and physical processes. Many pharmaceuticals exist as a form of crystalline hydrates, which is very important to maintain their chemical and physical stabilities. Dehydration of crystalline hydrates greatly impairs their stabilities as pharmaceuticals.[2] To understand the role of water, numerous crystallographic studies on hydrates of pharmaceuticals have been carried out.[2b,3] Therefore, elucidation of H-bonding patterns of water molecules in various surroundings is highly demanded. One of the definite ways of understanding the association of water molecules is the crystallographic study of small water clusters in organic hydrates. A large number of examples of water clusters have been reported in metal organic frameworks (MOFs). During the assembling process of coordination polymers under hydrothermal conditions, an infinite array of water networks can be created, owing to the coordination of water molecules to metals as a trigger to develop water clusters. Various types of water clusters can be generated with MOFs.[4] Metal-free organic hosts also afforded a number of water clusters.[5] Cyclic compounds are the typical examples, affording water clusters of large size. Circularly arranged heteroatom-containing frameworks behave efficiently as the scaffold to initiate hydrogen bonding with water molecules, leading to the formation of water clusters.

In the course of our study on imidazolium based ionic liquid crystals,[6] we found interesting crystal structures of hydrates of imidazolium salts in which water molecules were wedged into the two neighboring halide anions to act as a bridge to connect the two adjacent C−H···halide−anion networks of imidazolium moieties and counteranions.[7] The salts were found to exhibit a propensity to include water molecules. The results prompted us to investigate a series of salts by systematically changing the aromatic tether. As an effective H-bonding acceptor for water molecules, we employed a carboxylate as a counteranion attached to an imidazolium moiety. Two units of imidazolium carboxylate moieties were connected by an aromatic spacer to clip water molecules. Figure 1 illustrates an example of the method of clipping of water molecules by imidazolium carboxylate moieties as ionic clips. The way of sandwiching water molecules could depend on the size and shape of the spacer. A similar approach was reported using *trans*-bis(4-pyridyl)ethylene dioxide[5f] and protonated phenazine-2,3-diamine cation selenate salt[8] as hosts. In addition to the strong H-bonding ability of terminal carboxylate anion toward crystalline water, our zwitterionic imidazolium carboxylates have the following special features: (1) the imidazolium positive charge (C−H) can attract water molecule using charge assisted strong H-bonding, and (2) stacking of aromatic spacer groups creates a hydrophobic wall to confine water molecules.

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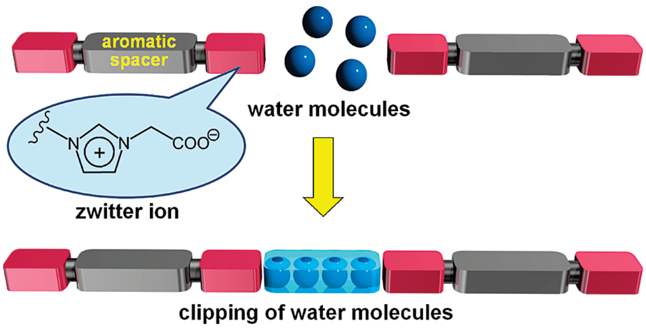
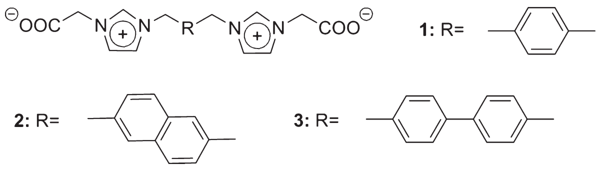


Figure 1. Schematic representation of the clipping of water molecules by imidazolium carboxylate moieties as ionic clips.

Chart 1. Biszwitterionic Imidazolium Salts Examined



Zwitterionic imidazoliuim carboxylates have been used as precursors for the preparation of halogen-free carboxylic acid functionalized imidazoliums.[9] Zwitterionic imidazolium salts are known as potential ion-conductive ionic liquids.[10] A number of crystal structures of imidazolium salts have been reported.[9,11] However, little is known about the crystal structures of zwitterionic imidazoliums.[12] The single crystal X-ray structure of 2-(1-(carboxymethyl)-1*H*-imidazol-3-ium-3-yl)acetate, a rare example of a zwitterionic imidazolium possessing a carboxylate as a counteranion, showed the existence of strong intermolecular O···H−O hydrogen bonding between CH_2COO^- and CH_2COOH moieties.[12a] Owing to this hydrogen bonding, a linear array of polymeric structure was created.

As spacers to connect two imidazolium carboxylates, we choose aromatic moieties, 1,4-phenylene, naphthalene-2,6-diyl, and biphenyl-4,4′-diyl, because of their rigidity and linearity. Herein, we report on our methodology for the formulation of various types of water clusters employing zwitterionic imidazolium carboxylates.

Imidazolium carboxylates **1**−**3** were prepared from hydrolysis of the corresponding ethyl ester derivatives followed by the treatments with triethylamine. Recrystallization from water with diffusion of acetone vapor afforded their single crystals, which were subjected to X-ray structural analysis.[13]

Figure 2a shows the packing diagram of the hydrate of **1** viewed along the *b* axis of the unit cell. In its crystals, water molecules were included in the molar ratio **1**/H_2O = 1:5. It showed that H-bonded water molecules were sandwiched between two neighboring carboxylate moieties via H-bonding.[14] The O···O distances are ca. 2.75−3.17 Å (see Table S1 in the Supporting Information). An infinite linear array of water tetramers was constructed in the direction of the *b* axis (Figure 2b). Imidazolium carboxylate **1** connects the 1D chains and forms a layer. Thus, a water channel structure was constructed via H-bonding and a CH/O interaction network in the crystal. Figure 2d shows an illustration of water channels created in the crystal. In addition, another type of inclusion of water molecules was observed in the crystal. Isolated water molecules were sandwiched between two neighboring carboxylate moieties via H-bonding with the O···O distance of ca. 2.71 Å (Figure 2c). The isolated water molecules were also fixed via CH/O interaction with acidic hydrogen atoms at the 2-position of imidazolium moieties. (The C···O distance is ca. 3.13 Å.)

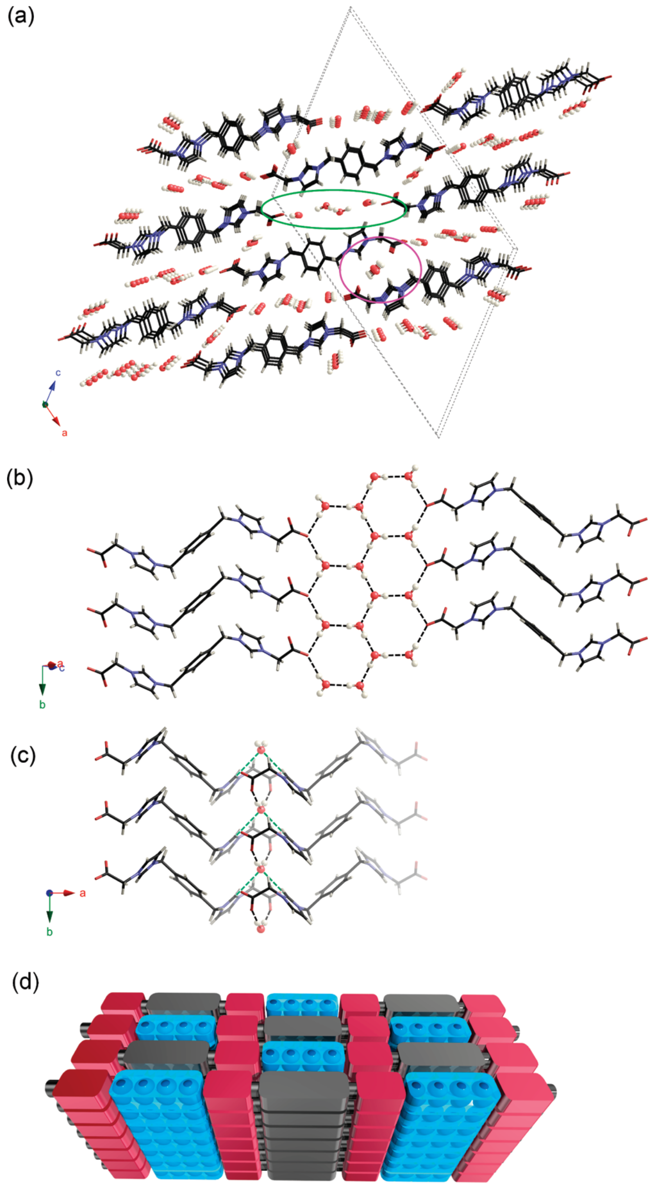


Figure 2. Packing diagram of crystal **1**·$5H_2O$ and an illustration of the water channels generated: (a) view along the *b* axis; (b) side view of the array of the water tetramer (green circle in part a) (H-bonds are indicated with black dotted lines); (c) side view of the isolated water molecules (magenta circle in part a) (CH/O interactions are indicated with green dotted lines, respectively); (d) illustration of the water channels.

The imidazolium carboxylate **2** showed pseudopolymorphs affording two types of crystals: needles and plates. Single crystal X-ray structural analysis of the needle showed that it contained water molecules in the molar ratio **2**/H_2O = 1:4.[14] Figure 3a shows that water dimers are sandwiched with the two neighboring carboxylates in the crystal. They form a 1D chain of waters. Single-file arrangements of water molecules in confined environments such as the channels of biological

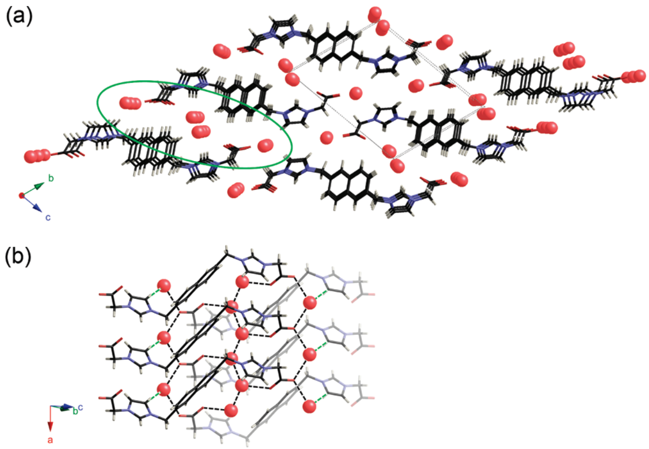


Figure 3. Packing diagram of crystal $\mathbf{2}\cdot4H_2O$: (a) view along the *a* axis; (b) side view of the 1D array of water dimers and isolated water molecules (green circle in part a). H-bonds and CH/O interactions are indicated with black and green dotted lines, respectively. The hydrogen atoms of water molecules are omitted for clarity.

membranes,[15] the interior of carbon nanotubes,[16] and the channels of hydrophobic tubular peptides[17] have been paid special attention in relation to proton transfer. The former possesses an inner polar lining, while the latter two have hydrophobic ones. The imidazolium carboxylate **2** provides confined polar channels suitable for 1D water chains. Similar zwitterionic water channels of narrow pore size were created by MOFs containing imidazolium carboxylates. Zinc-coordinated imidazolium carboxylates afforded a polymeric helical tube encapsulating a 1D water chain.[9b,18]

In addition to the array of water dimers, channels exist for arrays of isolated water molecules linked by H-bonding with the carboxylate moieties (Figure 3b). The water channels are along the *a* axis of the unit cell. Various interactions are observed between the water molecules and **2**. The O···O distances for H-bonding among water molecules in the channel are ca. 2.74 and 2.87 Å (see Table S2 in the Supporting Information). The O···O atomic distances for H-bonding between water molecules and carboxylate moieties are in the range ca. 2.70−2.83 Å. Water molecules have CH···O interactions with the hydrogen atoms of the imidazolium with the C···O distances in the range ca. 3.21−3.40 Å. In contrast to a 1D array of water dimers in the needle crystal of **2**, the plate crystal of **2** has a layer structure of a water hexamer (Figure 4a). Water molecules are included in the molar ratio $\mathbf{2}/H_2O$ = 1:5.5 in the crystal lattice.[19] The O···O distances for H-bonding among water molecules in the layer are in the range of ca. 2.73 and 2.80 Å (see Table S3 in the Supporting Information). Water layers are located between the layers of **2** (Figure 4b). Imidazolium carboxylates **2** are stacked and incline to the water layer. Each carboxylate moiety is H-bonded with water molecules with the O···O atomic distances in the range of ca. 2.70−2.91 Å (Figure 4c). The angle between the molecular axis of **2** and the water layer is ca. 25°, and the layer distance is ca. 8 Å.

Similarly, a zwitterionic water channel is created in the hydrate of **3**. Water molecules are included in the molar ratio $\mathbf{3}/H_2O$ = 1:4 in the crystal lattice.[19] Chiral crystals (space group $P2_1$) of $\mathbf{3}\cdot4H_2O$ were obtained from achiral **3**. Figure 5a shows that only one type of the channel structure exists in the crystal. In the channel structure, four molecules of water were linked with H-bonding discretely (Figure 5b).

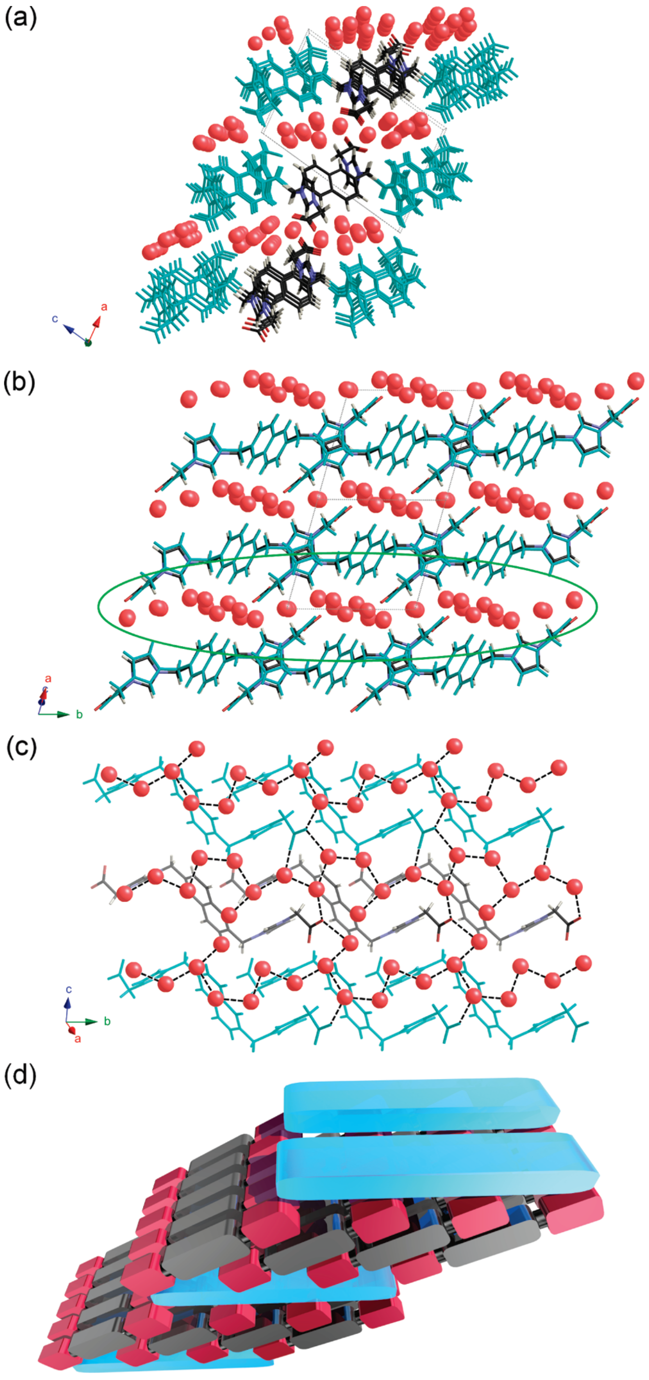


Figure 4. Packing diagram of crystal $\mathbf{2}\cdot5.5H_2O$: (a) view of the stacked water layers along the *b* axis; (b) side view of the stacked structure; (c) top view of the water layers (green circle in part b) (zwitterions **2** are colored in cyan except the representative molecules; H-bonds are indicated with black dotted lines); (d) illustration of the sandwiched water layers.

Figure 5c shows the H-bonding network of water molecules with the zwitterions. Each water molecule is H-bonded with the neighboring carboxylate moieties and the adjacent water molecule. The O···O atomic distances for H-bonding among water

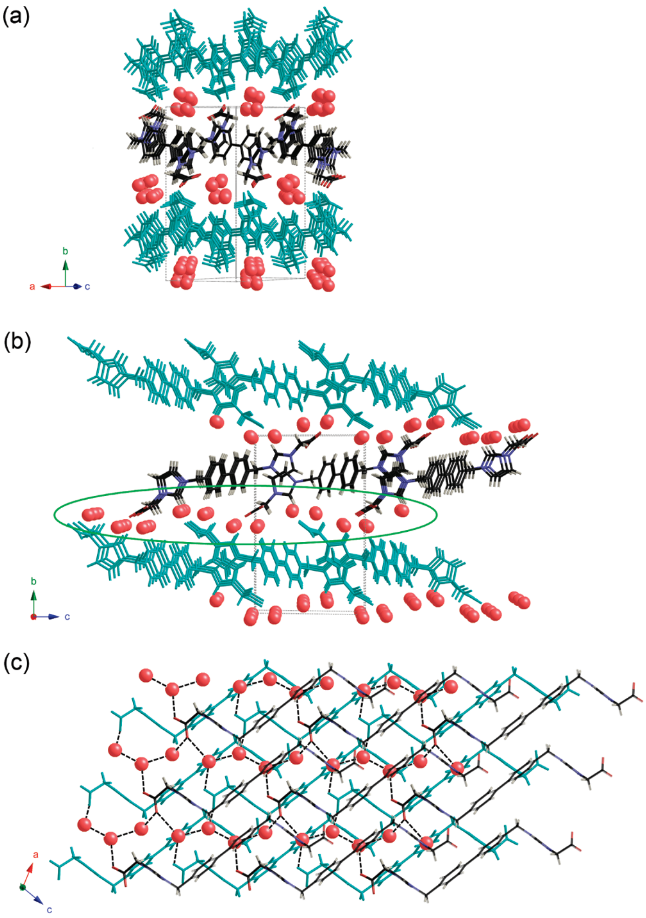


Figure 5. Packing diagram of crystal **3**·4H_2O: (a) view of the 1D channels including water molecules; (b) side view of the channel structure; (c) top view of the H-bonding network (green circle in part b). Zwitterions **3** are colored in cyan except the representative molecules. H-bonds are indicated with black dotted lines.

molecules are in the range ca. 2.77−2.88 Å (see Table S4 in the Supporting Information). Those between the oxygen atom of the water molecule and the carboxylate moieties are in the range ca. 2.71−2.94 Å.

As we have shown, biszwitterionic imidazolium carboxylates behave as good hydrogen bonding acceptors to clip water molecules to create zwitterionic water channels. Depending on the size and the shape of the aromatic spacers, water channels can be modified. Pseudopolymorphism originating in the way of stacking of aromatic spacers can also provide diversity in the type of generated water channels.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Preparation information and spectral data of **1**, **2**, and **3**, and the crystallographic information of **1**·5H_2O, **2**·4H_2O, **2**·5.5H_2O, and **3**·4H_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Buck, U.; Huisken, F. *Chem. Rev.* **2000**, *100*, 3863–3890. (b) Ludwig, R. *ChemPhysChem* **2000**, *1*, 53–56. (c) Ludwing, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1808–1827. (d) Head-Gordon, T.; Hura, G. *Chem. Rev.* **2002**, *102*, 2651–2670. (e) Infantes, L.; Motherwell, S. *CrystEngComm* **2002**, *4*, 454–461. (f) Keutsch, F.; Cruzan, J. D.; Saykally, R. J. *Chem. Rev.* **2003**, *103*, 2533–2577. (g) Mascal, M.; Infantes, L.; Chisholm, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 32–36. (h) Nangia, A. Water Clusters in Crystal Hydrates. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J. L., Steed, J. A., Eds.; Marcel Dekker: New York, 2007; Vol. 1, pp 1−9. (i) Fucke, K.; Steed, J. W. *Water* **2010**, *2*, 333–350.

(2) (a) Yu, L. *Adv. Drug Delivery Rev.* **2001**, *48*, 27–42. (b) Vogt, F. G.; Brum, J.; Katrincic, L. M.; Flach, A.; Socha, J. M.; Goodman, R. M.; Haltiwanger, R. C. *Cryst. Growth Des.* **2006**, *10*, 2333–2354.

(3) (a) Kiang, Y.-H.; Xu, W.; Stephens, P. W.; Ball, R. G.; Yasudas, N. *Cryst. Growth Des.* **2009**, *9*, 1833–1843. (b) Zhao, X. S.; Siepmann, J. H.; Xu, W.; Kiang, Y.-H.; Sheth, A. R.; Karaborni, S. *J. Phys. Chem. B* **2009**, *113*, 5929–5937. (c) Ruscica, R.; Bianchi, M.; Quintero, M.; Martinez, A.; Vega, D. R. *J. Pharm. Sci.* **2010**, *99*, 4962–4972. (d) Fujii, K.; Uekusa, H.; Itoda, N.; Hasegawa, G.; Yonemochi, E.; Terada, K.; Pan, Z.; Harris, K. D. M. *J. Phys. Chem. C* **2010**, *114*, 580–586. (e) Takata, N.; Takano, R.; Uekusa, H.; Hayashi, Y.; Terada, K. *Cryst. Grwoth Des.* **2010**, *10*, 2116–2122. (f) Clarke, H. D.; Arora, K. K.; Bass, H.; Kavuru, P.; Ong, T. t.; Pujari, T.; Wojtas, L.; Zaworotko, M. J. *Cryst. Growth Des.* **2010**, *10*, 2152–2167. (g) Lutker, K. M.; Quiñones, R.; Xu, J.; Ramamoorthy, A.; Matzger, A. J. *J. Pharm. Sci.* **2011**, *100*, 949–963.

(4) (a) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature* **1998**, *393*, 671–673. (b) Blanton, W. B.; Gordon-Wylie, S. W.; Clark, G. R.; Jordan, K. D.; Wood, J. T.; Geiser, U.; Collins, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3551–3552. (c) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Chem. Commun.* **2000**, 859–860. (d) Doedens, R. J.; Yohannes, E.; Khan, M. I. *Chem. Commun.* **2002**, 62–63. (e) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2003**, *42*, 8250–8254. (f) Ma, B.-Q.; Sun, H.-L.; Gao, S. *Chem. Commun* **2004**, 2220–2221. (g) Yoshizawa, M.; Kusukawa, T.; Kawano, M.; Ohhara, T.; Tanaka, I.; Kurihara, K.; Niimura, N.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 2798–2799. (h) Luna-García, R.; Damián-Murillo, B. M.; Barba, V.; Höpfl, H.; Beltrán, H. I.; Zamudio-Rivera, L. S. *Chem. Commun.* **2005**, 5527–5529. (i) Zuhayra, M.; Kampen, W. U.; Henze, E.; Soti, Z.; Zsolnai, L.; Huttner, G.; Oberdorfer, F. *J. Am. Chem. Soc.* **2006**, *128*, 424–425. (j) Wei, M.; He, C.; Hua, W.; Duan, C.; Li, S.; Meng, Q. *J. Am. Chem. Soc.* **2006**, *128*, 13318–13319. (k) Byrne, P.; Lloyd, G. O.; Clarke, N.; Steed, J. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 5761–5764. (l) Bai, S.-Q.; Hor, T. S. A. *Chem. Commun.* **2008**, 3172–3174. (m) Bi, Y.; Liao, W.; Zhang, H.; Li, D. *CrystEngComm* **2009**, *11*, 1213–1216. (n) Li, J.; Yu, J.; Xu, R. *Phys. Chem. Chem. Phys.* **2009**, *11*, 1291–1293. (o) Duan, C.; Wei, M.; Guo, D.; He, C.; Meng, Q. *J. Am. Chem. Soc.* **2010**, *132*, 3321–3330. (p) Sun, D.; Wang, D.-F.; Zhang, N.; Husang, R.-B.; Zheng, L.-S. *Cryst. Growth Des.* **2010**, *10*, 5031–5033. (q) Sang, R.-L.; Xu, L. *CrystEngComm* **2010**, *12*, 1377–1381.

(5) (a) Custelcean, R.; Afloroaei, C.; Vlassa, M.; Polverejan, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3094–3096. (b) Atwood, J. L.; Barbour, L. J.; Ness, T. J.; Raston, C. L.; Raston, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 7192–7193. (c) Moorthy, J. N.; Natarajan, R.; Venugopalan, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 3417–3420. (d) Sankaran, S. P. N. B.; Samanta, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1741–1743. (e) Raghuramna, K.; Katti, K. K.; Barbour, L. J.; Pillarsetty, N.; Barnes, C. L.; Katti, K. V. *J. Am. Chem. Soc.* **2003**, *125*, 6955–6961. (f) Ma, B.-Q.; Sun, H.-L.; Gao, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1374–1376. (g) Ghosh, S. K.; Bharadwaj, P. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 3577–3580. (h) Ma, B.-Q.; Sun, H.-L.; Gao, S. *Chem. Commun.* **2004**, 2220–2221. (i) Oxtoby, N. S.; Blake, A. L.; Champness, N. R.; Wilson, C. *Chem.—Eur. J.* **2005**, *11*, 4643–4654. (j) Lakshminarayanan, P. S.; Suresh, E.; Ghosh, P. *J. Am. Chem. Soc.* **2005**, *127*, 13132–13133. (k) Lakshminarayanan, P. S.; Suresh, E.; Ghosh, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3807–3811. (l) Kang, S. O.; Powell, D.; Day, V. W.; Bowman-James, K. *Cryst. Growth Des.* **2007**, *7*, 606–608. (m) Li, Y.; Jiang, L.; Feng, X.-L.; Lu, T.-B. *Cryst. Growth Des.* **2008**, *8*, 3689–3694. (n) Xu, W.-Z.; Sun, J.; Huang, Z.-T.;

Zheng, Q.-Y. *Chem. Commun.* **2009**, 171–173. (o) Saeed, M. A.; Wong, B. M.; Fronczek, F. R.; Venkatraman, R.; Hossain, M. A. *Cryst. Growth Des.* **2010**, *10*, 1486–1488. (p) Masu, H.; Sagara, Y.; Imabeppu, F.; Takayanagi, H.; Katagiri, K.; Kawahata, M.; Tominaga, M.; Kagechika, H.; Yamaguchi, K.; Azumaya, I. *CrystEngComm* **2011**, *13*, 406–409.

(6) Kohmoto, S.; Hara, Y.; Kishikawa, K. *Tetrahedron Lett.* **2010**, *51*, 1508–1511.

(7) Kohmoto, S.; Okuyama, S.; Nakai, T.; Takahashi, M.; Kishikawa, K.; Masu, H.; Azumaya, I. *J. Mol. Struct.* **2011**, *998*, 192–197.

(8) Sansam, B. C. R.; Anderson, K. M.; Steed, J. W. *Cryst. Growth Des.* **2007**, *7*, 2649–2653.

(9) (a) Fei, Z.; Zhao, D.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *Chem.—Eur. J.* **2004**, *10*, 4886–4893. (b) Fei, Z.; Ang, W. H.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *Chem.—Eur. J.* **2006**, *12*, 4014–4020.

(10) (a) Yoshizawa, M.; Hirao, M.; Ito-Akita, K.; Ohno, H. *J. Mater. Chem.* **2001**, *11*, 1057–1062. (b) Ohno, H.; Yoshizawa, M.; Ohihara, W. *Electrochim. Acta* **2003**, *48*, 2079–2083.

(11) (a) Broeke, J. V. D.; Stam, M.; Lutz, M.; Kooijman, H.; Spek, A. L.; Deelman, B.-J.; Koten, G. V. *Eur. J. Inorg. Chem.* **2003**, 2798–2811. (b) Zhao, D.; Fei, Z.; Scopelliti, R.; Dyson, P. J. *Inorg. Chem.* **2004**, *43*, 2197–2205. (c) Kölle, P.; Dronskowski, R. *Inorg. Chem.* **2004**, *43*, 2803–2809. (d) Gao, Y.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2004**, *43*, 3406–3412. (e) Fujimoto, T.; Nakakoshi, M.; Machinami, T.; Seki, H.; Nishikawa, K.; Tashiro, M. *Anal. Sci.* **2007**, *23*, x9–x10. (f) Reichert, W. M.; Holbrey, J. D.; Swatloski, R. P.; Gutowski, K. E.; Visser, A. E.; Nieuwenhuyzen, M.; Seddon, K. R.; Rogers, R. D. *Cryst. Growth Des.* **2007**, *7*, 1106–1114. (g) Alcalde, E.; Mesquida, N.; Vilaseca, M.; Alvarez-Rúa, C.; García-Granda, S. *Supramol. Chem.* **2007**, *19*, 501–509. (h) Gjikaj, M.; Brockner, W.; Namyslo, J.; Adam, A. *CrystEngComm* **2008**, *10*, 103–110. (i) Olivier, J.-H.; Camerel, F.; Selb, J.; Retailleau, P.; Ziessel, R. *Chem. Commun.* **2009**, 1133–1135.

(12) (a) Kratochvil, B.; Ondracek, J.; Velisek, J.; Hasek, J. *Acta Crystallogr.* **1988**, *C44*, 1579–1582. (b) Holbrey, J. D.; Reichert, W. M.; Tkatchenko, I.; Bouajila, E.; Walter, O.; Tommasi, I.; Rogers, R. D. *Chem. Commun.* **2003**, 28–29.

(13) (a) Crystal data for **1**·$5H_2O$: $C_{18}H_{28}N_4O_9$, M = 444.44, monoclinic, space group $C2/c$, a = 27.636(7), b = 4.744(1), c = 19.233(5) Å, β = 122.929(2)°, V = 2116.6(9) Å^3, Z = 4, D_{calcd} = 1.395 mg m^{-3}, T = 120 K, μ = 0.113 mm^{-1}, GOF on F^2 = 1.028, R_1 = 0.0381, wR_2 = 0.0813 ($I > 2\sigma(I)$), CCDC-803465. (b) Crystal data for **2**·$4H_2O$: $C_{22}H_{20}N_4O_4$, 2(H_2O), 2(O), M = 472.45, triclinic, space group $P\bar{1}$, a = 4.7129(13), b = 10.011(3), c = 12.908(4) Å, α = 69.426(3), β = 87.476(3), γ = 81.127(3)°, V = 563.3(3) Å^3, Z = 1, D_{calcd} = 1.393 mg m^{-3}, T = 100 K, μ = 0.108 mm^{-1}, GOF on F^2 = 1.051, R_1 = 0.0560, wR_2 = 0.1431 ($I > 2\sigma(I)$), CCDC-803467. (c) Crystal data for **2**·$5.5H_2O$: $C_{22}H_{20}N_4O_4$, 5.5(O), M = 492.42, triclinic, space group $P\bar{1}$, a = 9.5978(14), b = 9.7222(14), c = 13.736(2) Å, α = 85.692(2), β = 77.323(2), γ = 73.387(2)°, V = 1198.2(3) Å^3, Z = 2, D_{calcd} = 1.365 mg m^{-3}, T = 120 K, μ = 0.109 mm^{-1}, GOF on F^2 = 1.026, R_1 = 0.0592, wR_2 = 0.1602 ($I > 2\sigma(I)$), CCDC-803466. (d) Crystal data for **3**·$4H_2O$: $C_{24}H_{22}N_4O_4$, 4(O), M = 494.46, monoclinic, space group $P2_1$, a = 7.166(2), b = 16.621(5), c = 10.800(4) Å, β = 107.616(4)°, V = 1226.0(7) Å^3, Z = 2, D_{calcd} = 1.339 Mg m^{-3}, T = 120 K, μ = 0.102 mm^{-1}, GOF on F^2 = 0.993, R_1 = 0.0553, wR_2 = 0.1353 ($I > 2\sigma(I)$), CCDC-803468.

(14) The positions of hydrogen atoms of water molecules which were well-fixed via multi H-bonding in the crystal **1**·$5H_2O$ and **2**·$4H_2O$ were determined based on the electron density distribution.

(15) Agre, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4278–4290.

(16) (a) Nummer, G.; Rasaiah, J. C.; Noworyta, J. P. *Nature* **2001**, *414*, 188–190. (b) Alexiadis, A.; Kassions, S. *Chem. Rev.* **2008**, *108*, 5014–5034. (c) Cao, Z.; Peng, Y.; Yan, T.; Li, S.; Li, A.; Voth, G. A. *J. Am. Chem. Soc.* **2010**, *132*, 11395–11397.

(17) Raghavender, U. S.; Aravinda, S.; Shamala, N.; Kantharaju; Rai, R.; Balaram, P. *J. Am. Chem. Soc.* **2009**, *131*, 15130–15132.

(18) Zhaofu, F.; Zhao, D.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J.; Antonijevic, S.; Bodenhausen, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5720–5725.

(19) The positions of hydrogen atoms of water molecules in the crystal **2**·$5.5H_2O$ and **3**·$4H_2O$ were not determined.