Deep-Eutectic Solvents

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Versatile Structure-Directing Roles of Deep-Eutectic Solvents and Their Implication in the Generation of Porosity and Open Metal Sites for Gas Storage**

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Because of the unique integration of various properties such as excellent solvating properties, wide reaction temperature ranges, nonvolatility, and high thermal stability, ionic liquids have attracted increasing attention as solvents of choice for chemical synthesis.[1] In the past several years, the synthetic success using the ionothermal method has opened up a new route for the creation of novel inorganic and metal–organic framework materials.[2–7] Recently, Morris and Parnham reviewed this burgeoning area.[2b,h]

Some ionic liquids (ILs) such as 1-ethyl-3-methylimidazolium bromide are ionic compounds.[6] In addition to their solvent properties, the cations and anions of such ionic liquids can influence the synthetic process through direct incorporation (either individually or in combination) into crystal structures.[7]

There is also another type of ionic liquids: deep-eutectic solvents (DESs). Unlike ILs, DESs are mixtures for which the freezing point is lower than that of either of its two individual components. A DES consists of an ionic compound and a molecular compound. Examples of DESs include mixtures of quaternary ammonium salts (e.g., choline chloride) with neutral organic hydrogen-bond donors (such as amides, amines, and carboxylic acids).[5,8] As ionic liquids, DESs share many characteristics of conventional ILs. Furthermore, one advantage of DESs such as choline chloride/urea (or its derivatives) is their low cost, which makes DESs particularly desirable for applications in the large-scale synthesis of new functional materials.

As mixtures, DESs (three-component systems with cations, anions, and neutral ligands) are more complicated than ILs (two-component systems with anions and cations). In addition to cations and anions, DESs also contain neutral ligand molecules such as urea that can exert structure-directing effects. In this sense, DESs possess features of both ILs and molecular solvents. Each of the three individual DES components has the potential to participate in the self-assembly process, either individually or in combination with another component, making it possible to create new types of chemistry that are not accessible in either ILs or molecular solvents.

We are especially interested in DESs because they provide a unique route for the creation of porosity and coordinatively unsaturated metal centers, which have been shown to be desirable for enhancing gas-storage capacity and for promoting catalytic activity.[3,9] These properties stem from the strong tendency of the neutral ligand, which is an inherent part of the solvent, to bind to metal sites. Upon removal of such neutral ligands, both porosity and open metal sites can be created. Furthermore, as shown herein, the DES is recyclable, because the neutral ligand that serves as the template to generate porosity and open metal sites can be completely recovered through crystallization immediately after its removal from the pore. This recyclability represents an additional advantage of the method reported herein.

Prior to this work, DESs were shown to be effective solvents and structure-directing agents (SDAs) in the synthesis of a number of materials, generally with inorganic frameworks, such as various metal phosphates and phosphonates.[2e,f] Of particular interest is the recent demonstration by Morris and co-workers that unstable DESs can serve as template-delivery agents through decomposition.[2f] For example, 2-imidazolidinone (ethyleneurea) can decompose to deliver ethylenediamine, which in the protonated form can direct the formation of zeolite-type metal phosphates. In comparison, there has been relatively limited research on the use of DESs for the synthesis of metal–organic framework materials.[5] Because the reaction temperature used for the synthesis of metal–organic framework materials is usually lower than that used for the synthesis of inorganic frameworks (e.g., phosphates), we anticipate that DESs would be less likely to decompose and could therefore exert structure-directing effects that differ from those observed in the synthesis of metal phosphates.[2f]

Herein, we report a series of metal–organic frameworks synthesized using three deep-eutectic solvents (Scheme 1a). The self-assembly of the trivalent metals (In^{3+}, Y^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+}, and Yb^{3+}), 1,4-benzenedicarboxylate (bdc), and one or two components of a DES generates ten different materials in six distinct framework topologies (Table 1).

Of particular interest is the demonstration of the versatile structure-directing roles of DESs (Scheme 1b and Figure 1)

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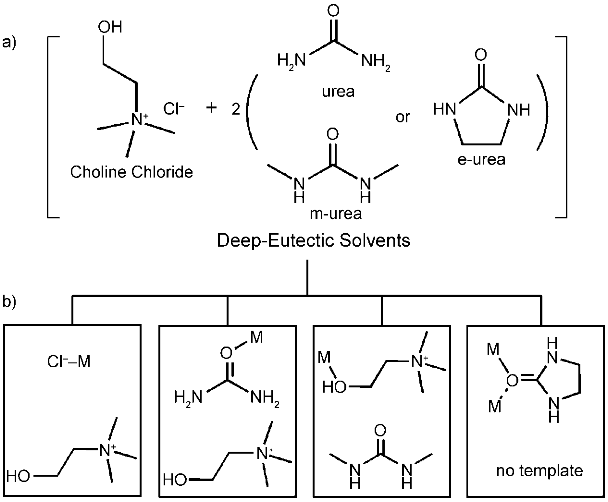


Scheme 1. a) The deep-eutectic solvents and b) their multiple roles (M = metal).

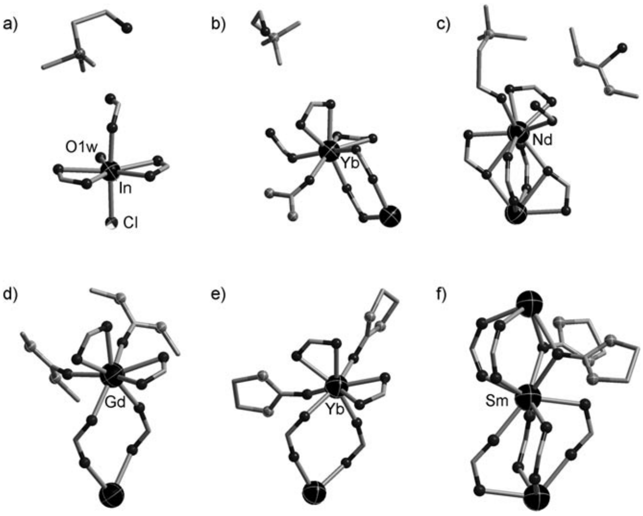


Figure 1. The coordination environment of the metal sites and the guest component in a) **1** (O1w = water oxygen atom), b) **2**, c) **3**, d) **4**, e) **5**, f) **6**. O black, N gray.

in addition to their role as solvent. The first role, observed in compound **1**, is the incorporation of both cations and anions. In **1**, cationic choline ions act as extraframework SDAs while the Cl^- ions are bound to the polymeric layers (Scheme 1 b, Figure 1 a).

In the second and third roles, cations and neutral ligands are incorporated into the structures. The incorporation of cations and neutral ligands results from the combined effect of the ionic compound and the neutral molecule in the DES. The second role is observed in three isostructural compounds **2**, **2a**, and **2b**, in which choline ions perform the same role as in compound **1** (i.e., as extraframework SDAs). However, neutral urea molecules (instead of Cl^- in compound **1**) are bonded to the framework (Scheme 1 b, Figure 1 b).

The third role, observed in compound **3**, is in fact the reverse of the second role, because choline ions are bonded to the framework through their OH groups, while the neutral m-urea molecules serve as extraframework SDAs (Scheme 1 b, Figure 1 c). Finally, the fourth role, observed in compounds **4**–**6**, is the direct bonding of neutral m-urea or e-urea to the polymeric framework (Scheme 1 b, Figure 1 d–f). Of these materials, **5**, **5a**, and **5b** are most closely related to the four-connected silica-type structures, because they possess moganite-type topology.

It is worth noting that nine out of ten materials reported herein contain the neutral DES component (urea, m-urea, or e-urea). This finding underlines the strong tendency for the incorporation of neutral ligands when the synthesis is performed in a DES. This incorporation forms the basis for the creation of porosity and open metal sites.

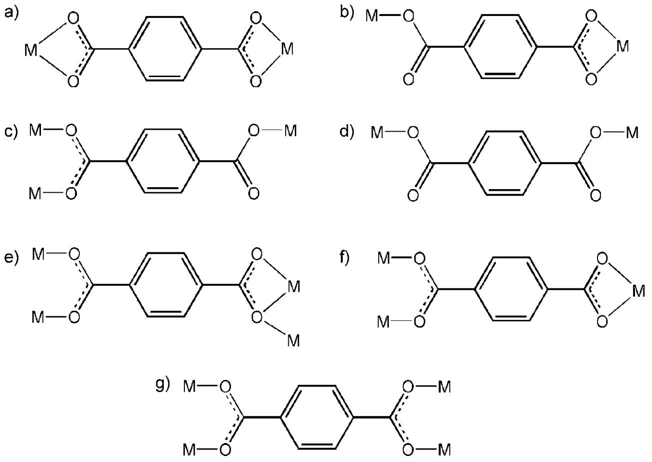
Compound **1** exhibits a 2D anionic (6,3) layer $[\{InCl(bdc)_{3/2}(H_2O)_2\}_n]^{n-}$, and the guest choline ions are located in the 1D channel (along the *c* axis) formed from adjacent layers by hydrogen-bonding interactions (Figure S1 in Supporting information).

Compounds **2**, **2a**, and **2b** are isostructural, and all of them exhibit similar 3D anionic frameworks that are charge-balanced by guest choline cations. In **2**, three independent bdc ligands adopt two coordination modes (Scheme 2 a, c). The urea ligand uses the O donor to coordinate to the Yb^{3+} site, and its two amino groups form N–H···O hydrogen bonds with the adjacent bdc ligands (Figure 1 b). Each eight-coordinate Yb^{3+} site is connected by two μ_2-bdc ligands and three μ_3-bdc ligands, resulting in the formation of a 3D framework with large 1D channels along the *b* axis (Figure 2 a). The quadrangular channel with dimension of 10.89 × 14.85 Å^2 is filled with guest choline cations. By reducing the μ_3-bdc ligands as

Table 1: Summary of crystal data and refinement results.[a]

Compound	Formula	Space group	*a* [Å]	*b* [Å]	*c* [Å]	α [°]	β [°]	γ [°]	*R*(F)
1	$(choline)[InCl(bdc)_{3/2}(H_2O)_2]\cdot H_2O$	$P2_1/c$	10.6925(2)	17.6168(4)	12.1630(3)	90.00	114.025(2)	90.00	0.0538
2	$(choline)[Yb(bdc)_2(urea)]$	$P\bar{1}$	8.4034(1)	10.5334(1)	14.3515(1)	100.83(1)	103.41(1)	101.56(1)	0.0191
2a	$(choline)[Sm(bdc)_2(urea)]$	$P\bar{1}$	8.3898(1)	10.6559(2)	14.3877(2)	101.964(1)	102.864(1)	102.681(1)	0.0206
2b	$(choline)[Y(bdc)_2(urea)]$	$P\bar{1}$	8.3734(2)	10.5740(2)	14.3077(3)	101.478(1)	103.120(1)	102.247(1)	0.0390
3	$[Nd(bdc)_2(choline)]\cdot(m\text{-}urea)$	$P2_1/n$	14.4400(3)	12.2290(2)	14.5152(3)	90.00	104.657(1)	90.00	0.0482
4	$[Gd_2(bdc)_3(m\text{-}urea)_4]$	$P2_1/n$	8.8307(3)	13.7279(4)	18.6260(5)	90.00	94.452(2)	90.00	0.0312
5	$[Yb_2(bdc)_3(e\text{-}urea)_4]$	$P\bar{1}$	9.7863(7)	10.2967(7)	11.0263(7)	76.898(5)	76.240(5)	65.487(5)	0.0301
5a	$[Dy_2(bdc)_3(e\text{-}urea)_4]$	$P\bar{1}$	9.8283(1)	10.4362(1)	11.0760(1)	76.894(1)	76.296(1)	65.999(1)	0.0158
5b	$[Ho_2(bdc)_3(e\text{-}urea)_4]$	$P\bar{1}$	9.8113(2)	10.4188(2)	11.0768(2)	76.721(1)	76.242(1)	65.932(1)	0.0176
6	$[Sm(bdc)_{3/2}(e\text{-}urea)]$	$C2/c$	20.8389(2)	10.6902(1)	16.3858(2)	90.00	111.973(1)	90.00	0.0223

[a] bdc = 1,4-benzenedicarboxylate; choline = $[(CH_3)_3NCH_2CH_2OH]^+$; m-urea = *N*,*N'*-dimethylurea; e-urea = 2-imidazolidinone (ethyleneurea).



Scheme 2. The observed coordination modes of the bdc ligand.

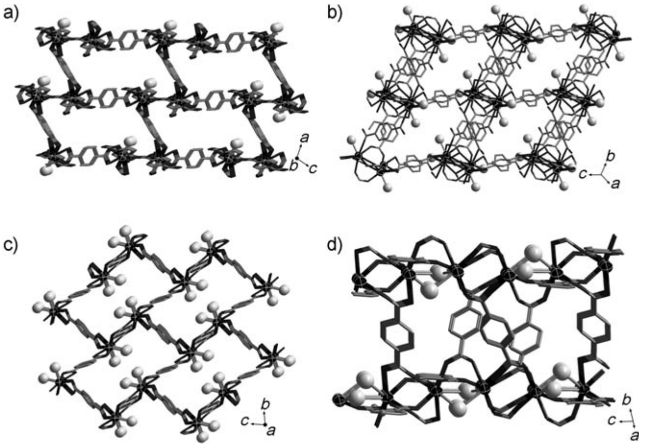


Figure 2. View of the 3D frameworks of compounds a) **2**, b) **3**, c) **5**, d) **6**. The components of the DES attached to each framework are omitted for clarity, and the potential binding sites of metals in each framework are shown as gray spheres.

the three-connected nodes and the Yb^{3+} sites as the five-connected nodes, the anionic framework of **2** can be represented as a (3,5)-connected net with the Schläfli symbol $(4^2.6^5.8^3)(4^2.6)$.[10]

Compared to the anionic frameworks of compounds **1, 2, 2a**, and **2b** prepared from the choline chloride/urea DES, compounds **3**–**6** were made using DESs containing the larger urea derivatives (m-urea and e-urea) and have neutral frameworks.

The most unusual feature of compound **3** is that the positively charged choline ion serves as a ligand bonded to a metal cation, while neutral m-urea acts as an extraframework template. Such a reversal of roles (cf. compound **2**) between the neutral urea-type ligand and the choline cation is quite unusual. Compound **3** features an eight-connected CsCl-type network based on dinuclear Nd^{3+} units. The bdc ligands adopt three different coordination fashions (Scheme 2a, d, e) to link the dinuclear Nd^{3+} units. Each Nd^{3+} ion is nine-coordinate, bound by eight O atoms from six bdc ligands and one O atom from the choline ion (Figure 1c). Each dinuclear Nd^{3+} unit is connected to eight adjacent dinuclear Nd^{3+} units by eight bdc ligands, resulting in an eight-connected framework with 1D channels filled with the guest m-urea molecules and dangling choline ions (Figure 2b).

Compound **4** is also synthesized using the choline chloride/m-urea DES. However, in contrast to **3**, only m-urea from the DES is included in the crystal. In **4**, each dinuclear Gd^{3+} unit is bound by four m-urea ligands and six bdc ligands with two types of coordination (Figure 1d, Scheme 2a, f). The connectivity between the dinuclear Gd^{3+} units and the bdc ligands generates a neutral six-connected (3,6)-sheet (Figure S6 in the Supporting Information).

The use of e-urea leads to a distinct neutral 3D framework **5**, also with only the neutral ligand, as in **4**. Three independent bdc ligands in **5** adopt two coordination geometries (Scheme 2a, f), and all are related by inversion. Each Yb^{3+} site in **5** acts as a four-connected node (Figure 1e) and is connected by four bdc ligands into a 3D framework with large 1D channels along the *a* axis (Figure 2c). By considering the μ_4-bdc ligands as the planar four-connected nodes, the framework of **5** can be represented as the four-connected moganite (denoted: mog) net. Thus, the use of DESs provides an alternative path for constructing low-connectivity frameworks from metal centers with high coordination numbers.

The replacement of $\mathrm{Yb(NO_3)_3}\cdot x\,\mathrm{H_2O}$ by $\mathrm{Dy(NO_3)_3}\cdot x\,\mathrm{H_2O}$ or $\mathrm{Ho(NO_3)_3}\cdot x\,\mathrm{H_2O}$ allows the preparation of the isostructural compounds **5a** and **5b**, respectively. On the other hand, the use of $\mathrm{Sm(NO_3)_3}\cdot x\,\mathrm{H_2O}$ under similar conditions gives a distinct structure **6**. The observation of two different structures (compound **5** from Yb^{3+} and compound **6** from Sm^{3+}) using the DES with e-urea is in distinct contrast to isostructural compounds **2** (Yb^{3+}) and **2a** (Sm^{3+}), thus demonstrating that the nature of the DES plays an important role in the self-assembly process.

The e-urea ligand in **6** adopts a μ_2-bridging mode, and two e-urea ligands doubly link two symmetry-related eight-coordinate Sm^{3+} sites with a Sm···Sm distance of 3.959 Å. Each Sm^{3+} site is bonded to six O atoms from six bdc ligands and two O atoms from two e-urea ligands (Figure 1f). The Sm−O bonds (2.533 and 2.607 Å) between Sm and the e-urea ligand are longer than those between Sm and the bdc ligand (average 2.391 Å). The carboxylate groups of the bdc ligands exhibit the same μ_2-bridging coordination (Scheme 2f) and connect Sm^{3+} sites into a chain along the *c* axis. Two O donors of two e-urea ligands complete two sites of the half-paddle-wheel dinuclear unit. Each carboxylate-bridged Sm chain is further linked to six neighboring chains by the bdc ligands to generate a 3D neutral framework (Figure 2d). The framework topology can be represented as a (4,6)-connected net by reducing the bdc ligand as the planar four-connected node and each Sm^{3+} site as a six-connected node. The Schläfli symbol of this three-nodal (4,6)-connected net is $(4^2.6^3.8)(4^3.6^3)_2(4^8.6^6.8)_2$.[10]

Compound **6** has a very high thermal stability and was selected to demonstrate the porosity and gas-storage properties of materials accessible through synthesis in DESs. Thermal gravimetric analysis (TGA) of **6** indicates that the first weight loss of 17.7% between 250 and 300°C corresponds to the full liberation of e-urea molecules (without decomposition; calcd: 17.8 %), and the remaining framework [{Sm(bdc)$_{3/2}$}$_n$] shows no weight loss up to 525 °C.

Powder X-ray diffraction further confirms that the framework [{Sm(bdc)$_{3/2}$}$_n$] does not change after the removal of the e-urea ligands at 300 °C (the degas temperature), and the total solvent-accessible volume is estimated to be 36.0 % using the PLATON program.[11] It is worth noting that the departure of the μ_2-e-urea ligand leaves two neighboring open Sm sites (Figure 3 a). The e-urea that escaped from the pores under the degas conditions crystallized at the cold end of the sample tube.[12] This finding suggests that the ligand is completely recyclable.

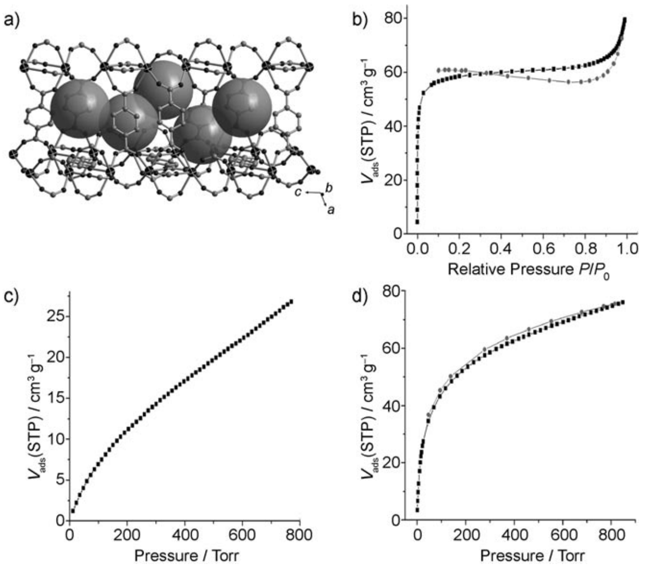


Figure 3. a) The porosity (highlighted by large gray spheres) of **6** and adsorption isotherms for its uptake of b) N_2, c) CO_2, and d) H_2. ■ adsorption, ● desorption. P/P_0 is the ratio of gas pressure (P) to saturation pressure (P_0), with $P_0 = 769$ torr.

Gas adsorption measurements (N_2, CO_2, and H_2) were performed on a Micromeritics ASAP 2010 surface-area and pore-size analyzer, which confirmed the permanent microporosity of **6**. The sample was degassed at 300 °C prior to the measurement. The N_2 adsorption/desorption study reveals a reversible type I isotherm, indicating that **6** is microporous (Figure 3 b). The BET and Langmuir surface areas are 186.3 and 261.5 m^{2}g, respectively. A diameter of 8.0 Å was also calculated.

The CO_2 adsorption isotherm of **6** at 273 K exhibits the adsorption of 26.8 cm^3 g^{-1} at approximately 1 atm (Figure 3 c). It is worth noting that increased uptake is accompanied by an increase in pressure, and the adsorption capacity does not saturate at 1 atm. Therefore, the uptake of CO_2 is expected to continue to increase at higher pressure.

The H_2 adsorption isotherm of **6** indicates an uptake of 74.9 cm^3 g^{-1} (0.66 wt %) at 77 K and 1 atm (Figure 3 d). Similar to the adsorption of CO_2, the hydrogen adsorption isotherm does not reach a plateau at 1 atm. Thus, a higher hydrogen uptake is expected under higher pressures. Although the hydrogen uptake is lower than those reported for many other porous frameworks, the use of a DES to generate porosity and free metal sites represents a new approach for the creation of porous metal–organic frameworks with potential applications in gas storage.

In summary, we report herein four different structure-directing roles of deep-eutectic solvents, leading to ten different materials with six distinct topologies. Using compound **6**, we demonstrate the high thermal stability, permanent porosity, and promising gas-storage capabilities of such materials. The synthetic method described herein provides a versatile path for the creation of porosity and open metal sites, thus allowing the synthesis of porous materials with potential applications in gas storage and catalysis. Also worth noting is the role of urea-type ligands, in this case e-urea, which acts as a template for framework formation and yet can leave the pore without any decomposition, leaving behind permanent porosity and open metal sites.

Experimental Section

The deep-eutectic solvents (choline chloride/urea, choline chloride/m-urea, and choline chloride/e-urea) were synthesized by heating a mixture of choline chloride and the urea compound in a 1:2 ratio at 120 °C for 20 min.

1: 1,4-Benzenedicarboxylic acid (H_2bdc, 0.0887 g, 0.53 mmol), 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.0622 g, 0.55 mmol), and $In(NO_3)_3{\cdot}x\,H_2O$ (0.0846 g, 0.21 mmol) in choline chloride/urea (2.03 g) were placed in a 20 mL vial. The sample was heated at 120 °C for 5 days and then cooled to room temperature. After washing with ethanol and distilled water, colorless crystals of **1** were obtained.

2: H_2bdc (0.0943 g, 0.57 mmol), DABCO (0.0747 g, 0.67 mmol), and $Yb(NO_3)_3{\cdot}x\,H_2O$ (0.1108 g, 0.24 mmol) in choline chloride/urea (2.172 g) were placed in a 20 mL vial. The sample was heated at 120 °C for 5 days and then cooled to room temperature. After washing with ethanol and distilled water, colorless crystals of **2** were obtained. Compounds **2a** and **2b** can be obtained under similar conditions using $Sm(NO_3)_3{\cdot}x\,H_2O$ (0.1289 g, 0.29 mmol) or $Y(NO_3)_3{\cdot}x\,H_2O$ (0.0982 g, 0.26 mmol) instead of $Yb(NO_3)_3{\cdot}x\,H_2O$.

3: H_2bdc (0.087 g, 0.52 mmol), DABCO (0.071 g, 0.66 mmol), and $Nd(NO_3)_3{\cdot}x\,H_2O$ (0.101 g, 0.23 mmol) in choline chloride/m-urea (2.30 g) were placed in a 20 mL vial. The sample was heated at 140 °C for 6 days and then cooled to room temperature. After washing with ethanol and distilled water, colorless crystals of **3** were obtained.

4: H_2bdc (0.083 g, 0.50 mmol), DABCO (0.060 g, 0.51 mmol), and $Gd(NO_3)_3{\cdot}x\,H_2O$ (0.115 g, 0.24 mmol) in choline chloride/e-urea (2.30 g) were placed in a 20 mL vial. The sample was heated at 140 °C for 6 days and then cooled to room temperature. After washing with ethanol and distilled water, colorless crystals of **4** were obtained.

5: H_2bdc (0.0883 g, 0.53 mmol), DABCO (0.0724 g, 0.66 mmol), and $Yb(NO_3)_3{\cdot}x\,H_2O$ (0.1118 g, 0.24 mmol) in choline chloride/e-urea (2.20 g) were placed in a 20 mL vial. The sample was heated at 120 °C for 4 days and then cooled to room temperature. After washing with ethanol and distilled water, colorless crystals of **5** were obtained. Compounds **5a** and **5b** can be obtained under similar conditions by using $Dy(NO_3)_3{\cdot}x\,H_2O$ (0.1102 g, 0.23 mmol) or $Ho(NO_3)_3{\cdot}x\,H_2O$ (0.1232 g, 0.24 mmol) instead of $Yb(NO_3)_3{\cdot}x\,H_2O$.

6: H_2bdc (0.1601 g, 0.99 mmol), DABCO (0.0980 g, 0.84 mmol), and $Sm(NO_3)_3{\cdot}x\,H_2O$ (0.1922 g, 0.46 mmol) in choline chloride/e-urea (3.50 g) were placed in a 20 mL vial. The sample was heated at 140 °C for 5 days and then cooled to room temperature. After washing with ethanol and distilled water, colorless crystals of **6** were obtained (0.195 g, 0.41 mmol, 88 %).

CCDC 707671 (**1**), 707672 (**2**), 707673 (**2a**), 707674 (**2b**), 707675 (**3**), 707676 (**4**), 707677 (**5**), 707678 (**5a**), 707679 (**5b**), and 707680 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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[12] Crystal data for e-urea: $C_3H_6N_2O$, $M_r = 86.10$, orthorhombic, space group *F*ddd, $a = 11.14(13)$, $b = 10.53(13)$, $c = 13.27(16)$ Å, $V = 1557(32)$ Å^3 , $Z = 16$, $\rho_{\text{cald}} = 1.470\ \text{g cm}^{-3}$, $R1(wR2) = 0.1394$ (0.3561) and $S = 1.164$ for 249 reflections with $I > 2\sigma(I)$. The crystal structure of e-urea is shown in Figure S15 in the Supporting Information.