1,4-Benzenedicarboxylate derivatives as links in the design of paddle-wheel units and metal–organic frameworks

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The square grid structure of MOF-2, constructed from paddle-wheel units of Zn(II) and 1,4-benzenedicarboxylate (BDC) links, persists for 2-amino-1,4-benzenedicarboxylate (ABDC) links but not for the sterically demanding 2,3,5,6-tetramethyl-1,4-benzenedicarboxylate (TBDC); the dihedral angle between planes of the benzene and carboxylate groups play a determining role in the formation of the paddle-wheel motif.

Extensive progress has been achieved in the synthesis of metal–organic frameworks (MOFs).[1–6] In particular MOFs of carboxylates have been designed to have permanent porosity in the absence of guests.[7–10] The first such material was constructed from paddle-wheel secondary building units (SBUs) and ditopic benzene links.[7a] Namely, Zn(BDC)·(DMF)(H$_2$O) (termed MOF-2) in which the benzene ring of BDC (1,4-benzenedicarboxylate) (Fig. 1a) is essentially in the same plane as the carboxylates (dihedral angle, $\Theta = 5.5°$), a feature that allows the formation of a porous 4^4 square network with one dimensional channels of 7.8 Å cross-section (Fig. 1a–c). Our interest in design of MOFs led us to consider whether other derivatives of BDC can form this structural motif. In particular we focused on 2-amino-1,4-benzenedicarboxylate (ABDC) and 2,3,5,6-tetramethyl-1,4-benzenedicarboxylate (TBDC), since the substituents on benzene were expected to result in rotation of the carboxylates out of the plane containing the benzene ring to give larger Θ. In this report, we show that the size of substituents, and Θ are critical parameters in the formation of paddle-wheel units and ultimately their reticulated MOFs.

The ABDC and TBDC compounds were prepared using identical procedures: slow diffusion of a mixture containing chlorobenzene–trimethylamine (700:1 v/v) into an N,N'-dimethylformamide (DMF)–chlorobezene (5/5 mL) solvent mixture containing Zn(NO$_3$)$_2$·6H$_2$O (55 mg, 0.185 mmol) and H$_2$ABDC (1 equiv.) or H$_2$TBDC (1 equiv.) at room temperature results after 4–7 days in the formation of Zn(ABDC)(DMF)·(C$_6$H$_5$Cl)$_{0.25}$ (MOF-46) or Zn$_2$(TBDC)$_2$(H$_2$O)$_{1.5}$(DMF)$_{0.5}$·(DMF)(H$_2$O), (MOF-47). These compounds were formulated and characterized by elemental microanalysis† and single crystal X-ray diffraction.‡

To fully appreciate the structures of MOF-46 and -47, it is important to consider first the structure of MOF-2 in which the paddle-wheel M–O–C core cluster is considered a square SBU (Fig. 1b) that is polymerized into square grids by benzene ditopic links (Fig. 1c). We sought to learn whether the paddle-wheel and thus the square grid can be produced from other BDC derivatives. Our approach required relating the dihedral angle, Θ of the benzene ring of the ligand to the distance, d between the
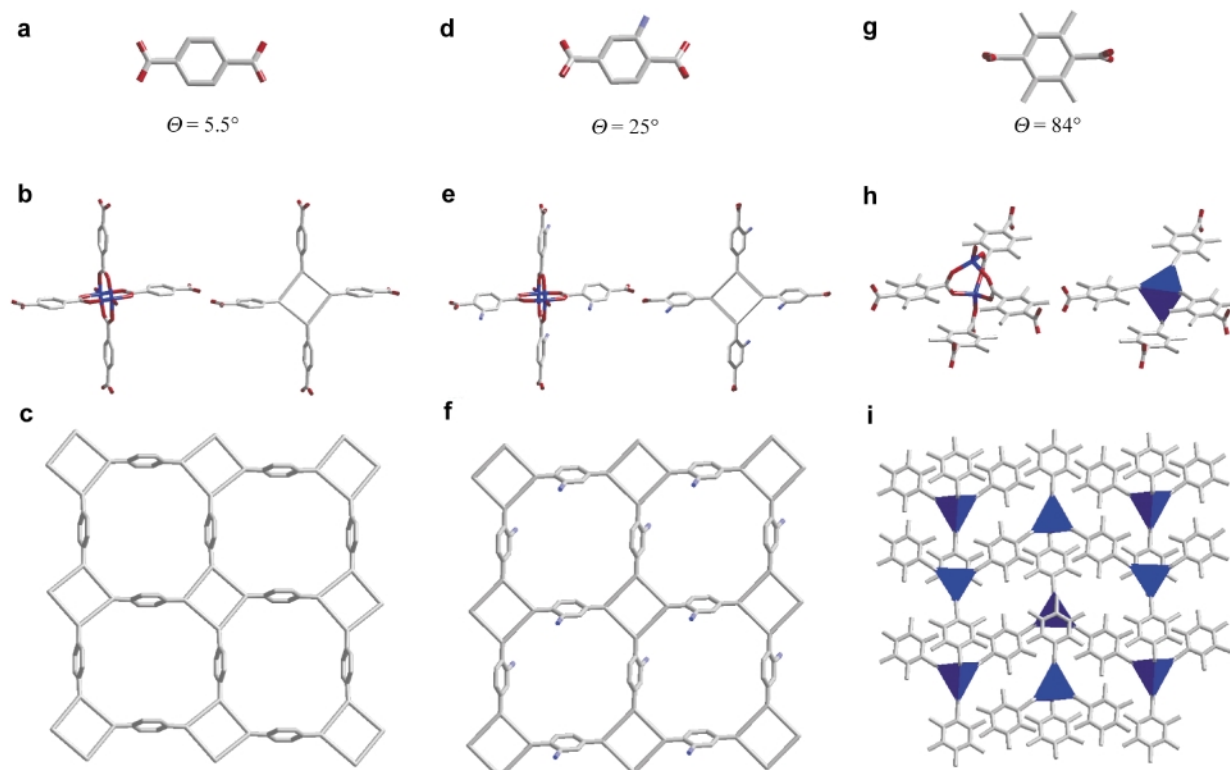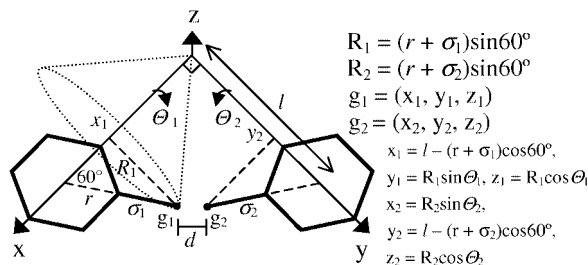

Fig. 1 The assembly of Zn(II) with BDC derivatives having a dihedral angle Θ to produce MOF-2 (a–c), MOF-46 (d–f) and MOF-47 (g–i). Zn(II) (blue) is connected to carboxylate O (red) with carboxylate C (gray) forming square (MOF-46) and tetrahedral (MOF-47) SBUs, which are linked by functionalized benzene units (N, light blue in d–f). All hydrogen atoms have been omitted for clarity.

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substituent groups (g_1 and g_2) of contiguous BDC units of the same paddle-wheel. This is illustrated below and d is derived accordingly.

The general equation for d can be obtained by using $d = \{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2\}^{1/2}$ with the limiting condition, $\{l(1 + \tan15°)\}/2 \geqslant R$. In case when g_1 and g_2 are the same functional groups and $(180° - \Theta_1) = \Theta_2$, this equation is simplified to $d = [2(l - (r + \sigma)/2 - \{3^{1/2}(r + \sigma)/2\}\sin\Theta_1)^2 + 3(r + \sigma)^2\cos^2\Theta_1]^{1/2}$.

$R_1 = (r + \sigma_1)\sin60°$
$R_2 = (r + \sigma_2)\sin60°$
$g_1 = (x_1, y_1, z_1)$
$g_2 = (x_2, y_2, z_2)$
$x_1 = l - (r + \sigma_1)\cos60°$,
$y_1 = R_1\sin\Theta_1$, $z_1 = R_1\cos\Theta_1$
$x_2 = R_2\sin\Theta_2$,
$y_2 = l - (r + \sigma_2)\cos60°$,
$z_2 = R_2\cos\Theta_2$

Here $l =$ the distance between the center of the SBU and the center of the benzene ring, $R =$ the radius of the trajectory of the circle generated by rotating the substituent group along the x- or y-axis by the dihedral angle, Θ. Thus to obtain a square grid structures as in MOF-2, functionalization of BDC should use groups that do not allow d to have value less than the summation of the van der Waals radii of g_1 and g_2.

For ABDC, $\Theta_1 = 25°$, $\Theta_2 = (180 - 25)°$, $l = 5.495$ Å, $r = 1.342$ Å and $\sigma = 1.40$ Å result in $d = 6.17$ Å which is enough to accommodate the $-NH_2$ groups. Then in principle, a paddle-wheel and an MOF-2 type structure can form. Reactions that are known to yield the paddle-wheel were utilized to make MOF-46. Indeed, the single crystal structure of the amino-benzene allows the formation of the expected motif (Fig. 1d–f), where the square layers are stacked along the c-axis, and DMF axial ligands fill the space in between adjacent layers. Due to the larger size of DMF relative to water (present in MOF-2 as an axial ligand), the $(CH_3)_2N-$ groups pertrude into the channels of MOF-46. In this way, the pores have periodic arrays of $(CH_3)_2N-$ and $-NH_2$ functionalities decorating the internal walls.

On the other hand, for TBDC, $\Theta_1 = 84°$, $\Theta_2 = (180 - 84)°$, $l = 5.309$ Å, $r = 1.398$ Å and $\sigma = 1.50$ Å result in $d = 2.00$ Å which is smaller than twice the van der Waals radii of the $-CH_3$ groups, 4.0 Å. Therefore it is not possible to produce an analogous framework. This is essentially a consequence of having methyl groups on both *ortho*-C atoms which inhibit the formation of the paddle-wheel structure at such a large dihedral angle. In fact, the van der Waals distance across the pores is 8.076–6.771 Å in MOF-2; well below that needed (9.329 Å) for TBDC units to replace BDC in that structure. Instead, MOF-47 is constructed from tetrahedral SBUs (Fig. 1g–i), a geometry known to be best in spacing apart sterically demanding groups.

Three carboxylate groups from three TBDC units are bound in a dimonodentate fashion to two Zn centers. One zinc center is also bound to a terminal water molecule, while the other is linked by an additional carboxylate in a monodentate fashion. Following the SBU structure analysis scheme, the carboxylate C atoms in the M–O–C cluster of MOF-47 forms a tetrahedral SBU. A closely related SBU is known in molecular complexes and other MOFs.[11,12] However, in this case, where it is expected that a tetrahedral SBU leads to the formation of a tetrahedral 4-connected 3-D network such as diamond, we find that the structure forms a double layer motif. Two TBDC units are bound entirely through dimonodentate coordination to Zn centers, and the remaining two units are each bound to Zn in

both dimonodentate and monodentate fashion. One water and one DMF molecule per formula unit fill the space between the layers.

Thermogravimetric analysis on MOF-46 and -47 show that the DMF ligands in MOF-46, and the guests in MOF-47 can be removed upon heating to > 50 °C: a weight loss of 41% was observed for MOF-46 in the range 50–310 °C corresponding to the loss of one DMF and 0.25 C_6H_5Cl (Calc.: 41%), and a sharper weight loss of 21% was measured for MOF-47 in the range 50–90 °C, which is attributed to the loss of 1.5 DMF and one water (Calc.: 21%). Both frameworks completely decompose above 350 °C.

This study demonstrates that the pores in MOFs can be functionalized with potentially reactive groups ($-NH_2$) without changing the SBU or the underlying framework topology (MOF-46). It is clear from the structure of MOF-47 that TBDC is too bulky to have the paddle-wheel arrangement or the square grid structure observed in MOF-2.

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