

## Inclusion of Thiazyl Radicals in Porous Crystalline Materials

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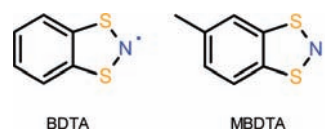
**S** Supporting Information

**ABSTRACT:** The incorporation of benzodithiazolyl (BDTA) and methylbenzodithiazolyl (MBDTA) radicals into porous hybrid frameworks *via* gas phase diffusion revealed that inclusion appeared selective for the MIL53-(Al) framework against a range of other potential hosts. Both PXRD and EPR studies are consistent with retention of a  $\pi^*-\pi^*$  dimer motif for BDTA in MIL53(Al)@BDTA whereas MBDTA in MIL53(Al)@MBDTA appears to be monomeric. The guests are readily released by the addition of solvent ( $\text{CH}_2\text{Cl}_2$ ).

Paramagnetic materials are an integral part of modern technology. For this reason, substantial research into materials with unique properties and characteristics is being continually performed by many groups worldwide. The extensive breadth of materials, from classical crystalline inorganic minerals to hybrid inorganic/organic systems, and from crystalline organic materials to soft materials made of organic polymers, indicates that no one class of material totally satisfies all technological niches.<sup>1</sup> One approach to tackle this problem is to develop hybrid materials in which the synergic interplay between different classes of material may ultimately afford novel types of behavior which are greater than the sum of the individual parts. In this article we report studies on the inclusion of thiazyl radicals into porous coordination-based frameworks. The production and physical properties of stable organic radicals have continued to be active areas of interest.<sup>2</sup> Among these, thiazyl radicals have shown particular promise as the inclusion of heavier *p*-block elements such as S and Se (in relation to O) offers greater dimensionality and magnetic anisotropy.<sup>3</sup> These favor higher magnetic ordering temperatures and a range of both magnetic and conducting materials as well as spin-transition materials have been reported in the literature.<sup>4</sup> Recent studies have implemented crystal engineering principles to control solid state architectures of thiazyl radicals in single-component systems<sup>5</sup> and drive formation of two component systems through the use of cocrystal formation.<sup>6</sup> The inclusion of thiazyl radicals into porous coordination materials has not previously been reported but offers the potential for magnetic communication between the radical guest and a paramagnetic framework, thereby modulating the magnetic properties of the host lattice; e.g. recent studies by Pöppel et al. have shown that the presence of a nitroxide radical modifies the magnetism of the copper framework  $\text{Cu}_3(\text{btc})_2$  (btc = benzenetricarboxylic acid).<sup>7</sup> Previous reports of thiazyl radicals acting as

guests within a host lattice have been limited to two inclusion complexes with the molecular organic perhydrotriphenylene (PHTP) host framework formed by cosublimation of host and guest. In both these cases the magnetic properties of the included radical were substantially modified, with the propensity for  $\pi^*-\pi^*$  dimerization<sup>2</sup> of the radical inhibited in both PHTP@*p*-NCC<sub>6</sub>H<sub>4</sub>CN<sup>SS</sup>N\* and PHTP@TTTA (TTTA = trithiazatriazeny).<sup>8</sup> These results indicate that there is potential for building more complex supramolecular architectures from thiazyl radicals in which the host fundamentally affects the supramolecular structure and subsequent behavior of the radical and, conversely, for the radical to modify the host. As an extension of this work we now report preliminary studies of the inclusion chemistry of thiazyl radicals within hybrid coordination-based frameworks.

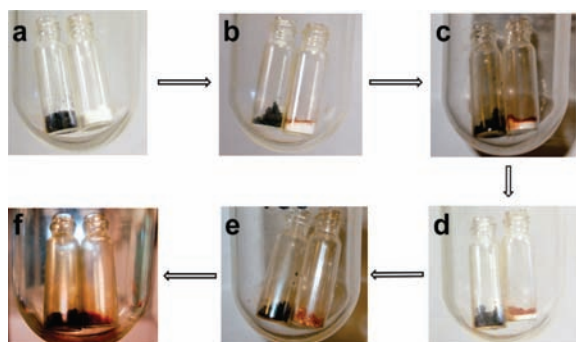
For these preliminary studies we used the known dithiazolyl radicals 5-methylbenzo-1,3,2-dithiazolyl (MBDTA) and benzo-1,3,2-dithiazolyl (BDTA) whose syntheses and solid state properties are well understood.<sup>4a,10a,9</sup> While BDTA adopts a *trans*-oid  $\pi^*-\pi^*$  dimer geometry in the solid state<sup>10</sup> linked *via* close S...S contacts (3.249 Å) and is diamagnetic, MBDTA is a paramagnetic monomer.<sup>9b</sup> A variety of porous coordination materials were examined as possible hosts: a transiently porous copper macrocycle material and a porous silver macrocycle material,<sup>11</sup> both of which undergo single-crystal-to-single-crystal desolvation; a flexible coordination polymer, MIL53(Al) (MIL = Materials of Institut Lavoisier),<sup>12</sup> and a stable porous material, ZIF8 (ZIF = zeolitic imidazolium framework).<sup>13</sup> MBDTA and BDTA were synthesized using known methods<sup>4a</sup> and the porous coordination compounds chosen for this study were synthesized using methods described in the literature.<sup>11-13</sup>



Previous work has shown that materials that are solid at room temperature can be included in coordination polymer frameworks *via* adsorption of the material directly from the gas phase: particularly relevant to the current study is the inclusion of ferrocene in MIL53(Al).<sup>14</sup> Attempted loading of radicals BDTA and MBDTA into the different host frameworks was performed by sublimation under vacuum.<sup>11b,15</sup> A small vial of radical (*ca.* 100 mg) and a small vial of porous material (*ca.* 100 mg) were

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**Figure 1.** Photographs of the conversion of MIL53(Al) to MIL53(Al)@MBDTA showing the sublimation under vacuum of the MBDTA (black solid) into the MIL53(Al) (white solid). Time exposed: (a) 0 h, (b) 24 h, (c) 46 h, (d) 72 h, (e) 96 h, and (f) 4 weeks. Note the diffusion of the radical into the MIL53(Al) sample (right) characterized by an increasing depth of brown coloration at the top of the sample.

placed in a Schlenk tube, which was then evacuated and heated at 50 °C to initiate sublimation of the radical. Using this technique we found that the copper macrocycle, silver macrocycle, and ZIF8 materials did not appear to the naked eye to undergo any change when exposed to either MBDTA and BDTA. This was confirmed by further analysis (mass spectrometry, PXRD, and UV, respectively). Conversely the MIL53(Al) framework underwent a clear change from a white powder when exposed to either MBDTA or BDTA, forming a reddish-brown and a dark-brown material respectively (Figure 1). The selectivity of the thiazyl guest for only the MIL53(Al) host likely arises from a combination of factors, not least of which is the well-known flexibility of the MIL53(Al) framework,<sup>12</sup> which may allow for easier diffusion of the radical into the pores of the host, and a good matching between the radical and pore shapes and sizes. The MIL53(Al)@MBDTA and MIL53(Al)@BDTA samples were characterized by UV/vis spectroscopy, powder X-ray diffraction (PXRD), and EPR spectroscopy to elucidate the properties and structure of these new hybrid materials.

The UV/vis transmission spectra of the MIL53(Al)@MBDTA and MIL53(Al)@BDTA samples are notably different from the pure BDTA and MBDTA samples and from the spectrum of pure MIL53(Al) (Figure S2). This is indicative of alteration in the packing of the radicals, which is to be expected in the restricted environment of the MIL53(Al) pores.<sup>15,16</sup> Freshly sublimed pure BDTA and MBDTA both show broad peaks across the UV/vis region with no discernible fine structure, as would be expected for their general dark color. The new MIL53(Al)@MBDTA and MIL53(Al)@BDTA materials also contain broad bands, but some fine structure becomes apparent within the 200 to 500 nm range (the pure MIL53(Al) material has only a sharp terephthalate-based absorbance peak at approximately 220 nm). The absorbance peaks for MIL53(Al)@BDTA (233, 295, 329, and 399 nm) are slightly blue-shifted in relation to the MIL53(Al)@MBDTA (238, 293, 347, and 411 nm). Additionally, MIL53(Al)@BDTA shows greater average absorbance than MIL53(Al)@MBDTA above 450 nm. These observations are in accordance with the variation in color between the two materials.

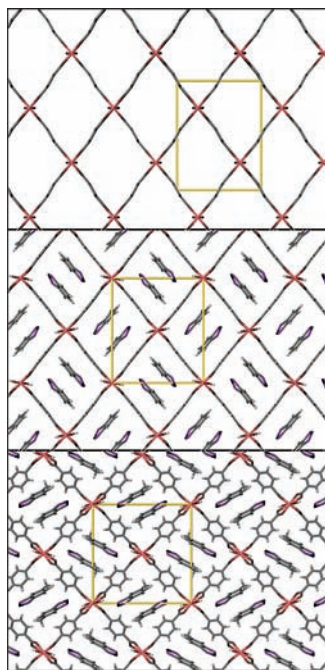
PXRD analysis reveals that both the MIL53(Al)@MBDTA and MIL53(Al)@BDTA materials exhibit clearly distinct powder patterns from that of the empty or hydrated MIL53(Al), indicative of a change in structure.<sup>12</sup> Further information on the structure of these materials was garnered by performing Pawley refinement

**Table 1.** Unit Cell Parameters for MIL53(Al), MIL53(Al)@BDTA, and MIL53(Al)@MBDTA

	MIL53(Al) <sup>12a</sup>	MIL53(Al)@BDTA	MIL53(Al)@MBDTA
space group	<i>Imma</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> (Å)	6.6085(9)	13.8911(7)	14.954(2)
<i>b</i> (Å)	16.675(3)	15.954(1)	15.089(2)
<i>c</i> (Å)	12.813(2)	6.6018(2)	6.6439(4)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	90	91.699(4)	90.819(6)
$\gamma$ (deg)	90	90	90
<i>V</i> (Å <sup>3</sup> )	1141.95	1462.5(1)	1499.0(3)

and simulated annealing on the powder patterns (using the program DASH),<sup>17a</sup> with final Rietveld refinement performed in Topas Academic.<sup>17b</sup> This pointed to a change in unit cell dimensions and space group of the MIL53(Al) framework for both inclusion materials, but no change in the chemical connectivity of the host framework (Table 1).<sup>12</sup> The inclusion of the radical within the channels of the host framework of MIL53(Al) resulted in a symmetry change from *Imma* (empty heated phase of MIL53(Al)) to *P2<sub>1</sub>/n*. The Al-to-Al distances defining a rectangular pore (related to the unit cell) changed from MIL53(Al) to (MIL53(Al)@BDTA) then (MIL53(Al)@MBDTA) becoming progressively more square: these distances are 16.68 and 12.81 Å in MIL53(Al), 15.94 and 13.90 Å in MIL53(Al)@BDTA, and 15.08 and 14.96 Å in MIL53(Al)@MBDTA (Figure 2).

Due to the significant contribution to the diffraction pattern by the sulfur-containing radicals, we were able to extract some information on the packing of the radicals within the pores of MIL53(Al). The guest radicals in both MIL53(Al)@BDTA and MIL53(Al)@MBDTA appeared well-located at specific sites within the channels, which offer a weak hydrogen bonded OH...N interaction between the nitrogen of the radical guest and the OH group of the host as well as  $\pi$ - $\pi$  interactions between the benzo-ring and the phenylene ring of the terephthalic acid. In addition the peak intensities could only be accurately reproduced assuming near full occupancy of the dithiazolyl radical sites (>85%). Both the simulated annealing and Rietveld refinement indicated that there may be some orientational disorder of the radical guests at those sites.<sup>18</sup> In both inclusion compounds, pairs of radicals are located around an inversion center but their displacements with respect to the inversion center lead to rather different structures. In MIL53(Al)@BDTA, the two rings are nearly eclipsed and separated by 3.297 Å, very close to the intradimer distances observed in dimeric  $\pi^*$ - $\pi^*$  dithiazolyl dimers (*cf.* 3.249 Å in BDTA). Such  $\pi^*$ - $\pi^*$  dimerization occurs *via* short intradimer S...S contacts [3.10–3.34 Å], and the location of the BDTA molecule with respect to the inversion center in MIL53(Al)@BDTA can only lead to such a  $\pi^*$ - $\pi^*$  dimer formation if the structure adopts a *cis*  $\pi^*$ - $\pi^*$  conformation which is permissible provided the molecule is disordered over two orientations. While BDTA itself adopts a *trans* conformation, several closely related BDTA derivatives adopt *cis* conformations<sup>19</sup> and the energy difference between them is very small [DFT B3LYP/6-31G\* indicates that the *cis* conformer is more stable by 14 kJ/mol]. In contrast, the MBDTA radicals in MIL53(Al)@MBDTA are considerably more offset with respect to the crystallographic inversion center,

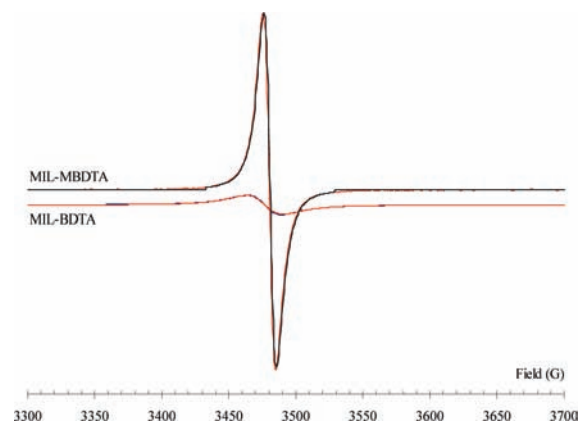


**Figure 2.** Empty MIL53(Al) structure is open (top) allowing for the diffusion of the radicals (middle BDTA, bottom MBDBTA) into the pore space resulting in changes in shape of the framework, and reorientation of the phenylene group of the terephthalate, and consequently the unit cells are related. MIL53(Al) viewed down *a* axis; MIL53(Al)@BDTA and MIL53(Al)@MBDBTA viewed down *c* axis.

and there is no evidence for  $\pi^*-\pi^*$  dimerization with the closest distances between radicals being C–H...S at 2.616 Å. The adoption of a  $\pi^*-\pi^*$  dimer motif in MIL53(Al)@BDTA but not in MIL53(Al)@MBDBTA is supported by EPR studies (see later).

In the case of MIL53(Al)@BDTA, the BDTA interacts with the aromatic rings of the terephthalate through  $\pi-\pi$  interactions (distance between centroids on aryl rings 3.768 Å). The good fit between the size of the BDTA and length of the terephthalate means pairs of BDTA radicals are included into the pore space. The inclusion of MBDBTA is similar to that of BDTA; however, the incorporation of the additional methyl group into the guest structure results in further distortion of the MIL53(Al) framework and a rotation of the phenylene group of the terephthalate.

EPR spectroscopy was used to probe the structures of both new radical-containing hybrid materials. The room temperature X-band EPR spectra of MIL53(Al)@MBDBTA and MIL53(Al)@BDTA both revealed isotropic singlet EPR spectra (Figure 3) with *g*-values comparable with previous solution studies on dithiazolyl radicals [MBDBTA in toluene *g* = 2.0065; BDTA in CFC<sub>3</sub> *g* = 2.008].<sup>9a,20</sup> Both spectra exhibited Lorentzian line shapes but revealed significant differences in both intensity and line width; MIL53(Al)@BDTA exhibited a significantly broader ( $\Delta H_{pp}$  = 23.4 G) but less intense resonance (~5%) than MIL53(Al)@MBDBTA ( $\Delta H_{pp}$  = 7.8 G). The broader and less intense line width of MIL53(Al)@BDTA is consistent with the structure determined by PXRD; disorder in the orientation of the BDTA molecule leads to either head-to-head or head-to-tail arrangements of radicals. When the radicals adopt a head-to-head configuration then this generates a singlet  $\pi^*-\pi^*$  dimer which is EPR inactive.<sup>4,10,9</sup> Conversely head-to-tail association of



**Figure 3.** Room temperature EPR spectra of polycrystalline MIL53-(Al)@BDTA (*g* = 2.0108,  $\Delta H_{pp}$  = 23.4 G) and MIL53(Al)@MBDBTA (*g* = 2.0095,  $\Delta H_{pp}$  = 7.8 G) (red) with simulated line shapes (black).

BDTA radicals inhibits dimer formation and will contribute to the EPR spectral intensity. The short intermolecular contacts between radicals (distance between C<sub>2</sub>S<sub>2</sub>N ring centroids = 4.086 Å) and the resultant dipolar interactions (which vary as  $r^{-3}$ ) are consistent with the broader nature of the EPR spectra. The steric demand of the additional methyl group in MBDBTA appears to hinder dimerization within the channels of MIL53-(Al)@MBDBTA (*cf.* the solid state structures of dimeric BDTA and monomeric MBDBTA, as well as inter-radical distances above).<sup>9</sup> The resultant distances between nearest neighbor C<sub>2</sub>S<sub>2</sub>N ring centroids now fall in the region 5.730–6.811 Å. As a consequence the EPR spectrum is an order of magnitude more intense than the BDTA-included complex and the line width is considerably narrower consistent with reduced dipolar broadening effects associated with the larger intermolecular contacts. Additional studies at 77 K revealed no change in spectral features.<sup>21</sup> When CH<sub>2</sub>Cl<sub>2</sub> was added to a sample of MIL53(Al)@MBDBTA or MIL53(Al)@BDTA, an isotropic 1:1:1 triplet EPR spectrum [*g* = 2.0102, *a<sub>N</sub>* = 11.3 G,  $\Delta H_{pp}$  = 2G (Lorentzian)] was observed consistent with regeneration of the dithiazolyl radical from the porous material (Figure S3), confirming its retention in the framework without degradation. Performing the same experiment but using mass spectrometry confirmed the release of the radical species (Figures S4 and S5). No degradation of the samples was noted when tested using PXRD, EPR, and MS, even when samples had been exposed to air at ambient conditions for at least three months. This enhanced stability of the radical within these hybrid materials is in stark contrast to the pure radicals which degrade when not kept under an inert atmosphere. These findings are consistent with recent studies which revealed that it is possible to generate radicals within the pores of coordination polymer frameworks, and these radicals were shown to be stable for up to a month.<sup>22,23</sup>

In conclusion, the incorporation of dithiazolyl radicals into the porous framework material MIL53(Al) leads to synergic interactions between host and guest structures, reflected in the modification of the host structure and localization of radicals so as to optimize host–guest interactions. The effect on the guest is to modify the  $\pi^*-\pi^*$  mode of association of BDTA from *trans* in pristine BDTA to *cis* in MIL53(Al)@BDTA and to lead to an increase in sample paramagnetism. In addition, we have shown that these radicals not only can be stabilized as a guest for extended periods but also can readily be released in a controlled



manner by simple exposure of the host–guest complex to a suitable solvent. Now armed with a better understanding of the binding of these guests in diamagnetic hosts, we are well-placed to extend these studies to inclusion into paramagnetic hybrid frameworks where there are rich opportunities for magnetic communication between host and guest species.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** UV/vis spectra, details of structure determination from PXRD patterns (CIFs), EPR data, and details of computational studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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