Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 9189



Luminescent infinite coordination polymer materials from metal-terpyridine ligation[†]

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Received 15th April 2011, Accepted 8th June 2011 DOI: 10.1039/c1dt10671f

A new class of infinite coordination polymers (CP) was synthesized using a tetrahedral tetrakis[4-(4'-phenyl-2,2':6',2"-terpyridine)phenyl]methane ligand as an organic node to direct the three-dimensional growth of the network and M^{II} (M = Zn, Fe, Ni, and Ru) ions as inorganic linkers, an approach that is the opposite of the metal-as-a-node strategy used in the construction of metal–organic frameworks (MOFs). The unusual rod-like morphology of the resulting microporous materials can be tuned *via* solvents and reaction conditions. The covalent entrapment of a [Ru(tpy)₂]²⁺ moiety in the skeleton of the 3D-network enables the Ru-CP to exhibit room-temperature luminescence.

Introduction

Microporous solids¹⁻¹² have attracted significant recent attention from the scientific and industrial communities13-17 given their wide array of potential applications. Specifically, these low-density solids have been utilized in catalysis,18,19 gas storage,20 and chemical separations,²¹ where their large internal surface areas provide a great advantage over non-porous alternatives. Among the wide range of microporous materials that have been reported, crystalline metal-organic frameworks (MOFs)^{1,2} are the most studied class, comprising organic spacers that serve as linkers between inorganic nodes to yield well-ordered, three-dimensional structures. Purely organic microporous solids, such as (crystalline) covalent-organic frameworks (COFs),²²⁻²⁵ (amorphous) polymers of intrinsic microporosity (PIMs),⁴ and (amorphous) porous organic polymers (POPs),²⁶⁻³² have also been prepared. In PIMs and POPs, the organic repeat units serve as both spacer and node, with microporosity resulting from the incorporation of 3D-directing monomers, the entanglement of highly crosslinked polymers, and/or the deployment of inherently poorly packed molecules as building blocks. More recently, the Suh group has shown that crystalline porous coordination polymers can also be constructed using an opposite approach to the construction of MOFs: tetrahedral methanetetrabenzoate (mtb) ligand was

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employed as a 3D-directing organic node and [Ni(cyclam)]²⁺ was employed as a metal-ion linker to afford a four-fold interpenetrating diamondoid network where the cyclam ligand remains on the Ni center after assembly.³³

To further explore the aforementioned strategy, we turned our attention to multi-terpyridine ligands, which have been utilized in the directed synthesis of metal-mediated, self-assembled metallomacrocycles and nonporous polymeric materials with novel photochemical and electronic properties.³⁴ We envisioned that a tetrahedral building block featuring four terpyridine groups would generate, in the presence of "naked" O_h metal centers, highly porous materials that have persistent luminescence even at room temperature, in contrast to homogeneous analogues. Herein, we report the synthesis and characterization of an amorphous, luminescent, microporous infinite coordination polymers (CPs) formed from the reaction of the rigid tetraterpyridine ligand 4 and transition metal ions such as Zn^{II}, Fe^{II}, Ni^{II}, and Ru^{II} (Fig. 1). The morphology of these materials can be tuned *via* ligand solubility and reaction conditions.

Results and discussion

The tetraterpyridine ligand **4** was easily obtained from 4'-(4bromophenyl)terpyridine³⁵ (1) in two steps (Scheme 1). Compound **1**, which is prepared from 4-bromobenzaldehyde and 2acetylpyridine, was first converted to the boronic ester **2** in high yield using Pd-catalyzed borylation.³⁶ Suzuki coupling of **2** and the tetrabromo core **3**³⁷ in a microwave reactor then afforded the desired building block **4** in 30% isolated yield. Prolonged reaction did not improve the yield of **4** due to the intrinsic low solubility of the partially substituted intermediates, which readily co-precipitate with the product and do not react further.

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[†] Electronic supplementary information (ESI) available. Experimental procedures for the synthesis of **1–4** and CPs, X-ray crystallography analysis of ligand **4**, TGA, FTIR, SEM images and CO₂ adsorption-desorption isotherms of CPs details. CCDC reference numbers 822508. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10671f



Fig. 1 Synthesis of hybrid porous coordination polymers featuring a tetrahedral rigid ligand-based nodes connected by single metal ions (Zn^{II}, Fe^{II}, Ni^{II}, and Ru^{II}). For visualization simplicity, the resulting solid is represented as an idealized diamond cubic network although multiple catenation occurred in reality (see discussion in the text).

The solvothermal reaction between 4 (2.0 mM) and two equivalents of Zn^{II}, Fe^{II}, Ni^{II}, or Ru^{II} salts, in EtOH, DMF, EtOH/DMF, or EtOH/MeCN (Fig. 1), readily yields the corresponding CPs. These solvents and solvent combinations were chosen to ensure good solubility of the initial terpyridine-metal complex thereby facilitating the formation of high molecular weight CPs. Reactions were performed in either a microwave reactor at 150 °C or by conventional heating at 90 °C for 20 or 50 h (Table 1). Although binding constants of the aforementioned metal ions to the terpyridine ligand are high (>108),38 heating is critical as it accelerates CP formation to afford high-molecular-weight polymers that eventually precipitate from solution. In the case of EtOH, heating also increases the solubility of the ligand at the beginning stage of the reaction and influences the morphology of the resulting solid (see discussion below). Upon heating, colored solutions were observed (dark purple for Fe^{II}, light yellow for Zn^{II} and Ni^{II}, and dark red for Ru^{II}), signifying (for Ru and Fe) the formation of terpyridine metal complexes featuring intense metalto-ligand charge-transfer (MLCT) band in the visible region. As the reaction proceeded, precipitates of the same color formed, leaving lightly colored (in the case of Ru^{II}) or clear solutions.

Table 1 Reaction conditions, yields, and surface areas of various CPs



Scheme 1 The synthesis of tetraterpyridine **4**. Shown on the bottom left is a ball-and-stick representation of the X-ray crystal structure of **4** (hydrogen atoms are omitted for clarity). The three pyridine rings in each terpyridine moiety showed a *transoid* arrangement about the interannular C–C bonds which is in good agreement with previous terpyridine crystal structures in the literature.^{39,40} Two of the four phenyl rings that are directly attached to the central pyridine are disordered (see CIF file that is part of the ESI[†]) but are not shown.

The metal content of the CPs, as measured by inductively coupled plasma optical emission spectroscopy (ICP-OES), is consistent with theoretical values (see ESI†), suggesting a stoichiometry of two metal ions per ligand. FT-IR spectra

Entry	Metal-CP Product ^a	Reaction Media	Isolated Yield (%)	Surface Area ^e (m ² g ⁻¹)
1	Zn_2-4 (NO ₂)	MeCN/EtOH ^{b,c}	96	410
2	$Zn_2 - 4$ (NO ₂) ₄	$MeCN/EtOH^{c,d}$	94	260
3	$Zn_2 - 4$ (NO ₂) ₄	EtOHd	91	360
4	$Zn_2 - 4$ (NO ₂) ₄	$DMF/EtOH^{c,d}$	89	250
5	$Fe_{2}-4$ Cl ₄	EtOH ^b	84	290
6	Fe_2-4 Cl ₄	EtOH ^d	87	490
7	Fe_2-4 Cl ₄	$DMF/EtOH^{c,d}$	85	380
8	Fe_2 -4 Cl ₄	DMF^d	81	450
9	Ni ₂ -4 Cl	EtOH ^b	86	300
10	Ni_2-4 Cl ₄	EtOH ^d	61	410
11	Ni ₂ -4 Cl ₄	$DMF/EtOH^{c,d}$	73	490
12	Ni ₂ -4 Cl ₄	DMF^d	92	330
13	$Ru_2 - 4 Cl_4$	EtOH ^b	81	430
14	$Ru_2 - 4 Cl_4$	EtOH ^d	8	NAf
15	Ru ₂ -4 Cl ₄	$DMF/EtOH^{c,d}$	71	480
16	$\mathbf{P}_{\mathbf{u}} \wedge \mathbf{C}_{1}$	DME^{d}	81	690

^{*a*} Total ligand concentration in the reaction mixture at the start is 2 mM. ^{*b*} Microwave irradiation at 150 °C, 20 h. ^{*c*} 1:1 v/v. ^{*d*} Conventional heating at 90 °C, 50 h. ^{*c*} Calculated from CO₂ adsorption isotherm using NLDFT slit pore model. ^{*f*} Low yield of the reaction did not produce enough material (2 mg) for an isotherm to be obtained.

(Figs. S4-8 in ESI[†]) further confirmed the proposed trischelating ligand structure, as the C=C stretch of the terpyridine moieties in 4 shifted from 1584 to 1600 cm⁻¹ after CP formation.⁴¹

Thermogravimetric analysis (TGA) of an as-synthesized Ni-CP sample (Table 1, entry 9; see also Fig. S11 in ESI[†]) exhibited ~15% solvent loss by weight, suggesting that this material is moderately porous. TGA profiles of all dry samples (Figs. S9-S12 in ESI[†]) demonstrated a wide range of thermal stability of the CPs, with the location of the degradation mass loss feature ranging from ~250 °C for Ru-linked samples to ~ 430 °C for Ni-linked samples. A few of the Fe-linked samples are stable past 550 °C. Such a broad range of stability can probably be attributed to the compatibility between the terpyridine ligand and the metal ions: the hard terpyridine ligand is better matched with the hard first-row metals such as Fe, Ni, and Zn than Ru. The variation in thermal stability for the Fe-linked samples (Fig. S10 in ESI[†]) can be further attributed to potential defects in these materials.

Samples prepared in different solvents, regardless of the linking metal ion, exhibit distinctly different textures. Those prepared in EtOH are light and powdery, while those prepared in DMF are chunky. Via scanning electron microscopy (SEM), a clear correlation between solvent system and morphology can be observed: all samples prepared in EtOH at 150 °C (microwave heating) exhibit long rod-like shapes with lengths extending well over 20 µm (Fig. 2, panels A-1, D-5, and G-9; although these rods appear crystalline, they do not diffract X-rays), while those prepared in DMF are solid masses lacking distinct features (Fig. S13,[†] panels D, E, F). When the temperature of the EtOH-based synthesis is dropped to 90 °C, the CP rods become shorter (~ 5 and 10 µm; Fig. 2, panels B-3, E-6, and H-10). In stark contrast to these well-defined particles, CPs prepared in equivolume EtOH/DMF

EtOH in MW @ 150 °C EtOH @ 90 °C EtOH/DMF @ 150 °C



We ascribe the aforementioned morphological differences to differences in solubility of 4 in the various solvent combinations. Based on the data in Fig. 2, the growth of CPs can likely best be described by a modified LaMer mechanism,⁴² where dissolved ligand serves as a nucleation site for particle growth. Since 4 is poorly soluble in EtOH, comparatively little will be accessible to the metal ions in solution during CP assembly. Not surprisingly, this results in a comparatively small number of comparatively large particles. When DMF is added to EtOH, the ligand becomes more soluble, providing the linking metal ions access to a higher concentration of organic nodes (nucleation sites), and affording a large number of small particles, as indeed observed. The nodes, as well as intermediate oligomeric complexes, are even more soluble in pure DMF, significantly increasing the number of coordinationcrosslinking reactions and leading to an amorphous mass at the end. This latter hypothesis is consistent with the observation that product from DMF-based reactions tends to precipitate more quickly. The ability to tune particle shapes and rod lengths via the solubility of the molecular component in different media mirrors those observed in nanoparticles43,44 and nanowires45 grown from Sn(porphyrin), as well as nanoparticles⁴⁶ and nanocubes⁴⁷ grown from metallosalens. In the syntheses of POPs where all of the reagents are soluble at the beginning of the reaction, spherical particles ranging from nano to micro size are generally observed.27,30,48

In contrast to $[Ru(tpy)_2]^{2+}$ complexes, which display almost no luminescence in solution at room temperature, the Ru-based CPs exhibit strong luminescence that can easily be observed in epi-luminescence images (Fig. 3). This solid-state luminescence is reminiscent of that for $[Ru(tpy)_2]^{2+}$ complexes that have been crystallized 49 or entrapped in Y zeolite, 50,51 and can be attributed



Fig. 3 (A) An optical image of Ru-CP (Table 1, entry 15). (B–D) Corresponding luminescence microscopy images of Ru-CP: (B) excitation at 490 \pm 20 nm and emitted at 685 \pm 40 nm; (C) excited at 360 \pm 40 nm and emitted at 457 ± 50 nm; and (D) excited at 490 ± 20 nm and emitted at 528 ± 38 nm. Scale bars = 20 μ m.



Fig. 2 SEM images of Zn-, Fe-, and Ni-CPs prepared under a variety

of reaction conditions (MW = microwaved). In each panel, the numbers

following the letter designations refer to the sample entries in Table 1. Scale

bars = 5 μ m. See Fig. S14 in ESI for the corresponding images of Ru-CPs.†

to the restriction that the solid state places on these complexes to reorganize for energy release from the photo-excited state. Such restriction only allows the "solidified" $[Ru(tpy)_2]^{2+}$ to luminesce at room temperature through an excited triplet MLCT state, in contrast to solution-phase analogue where nonradiative decay at room temperature is facilitated through an accessible ligand-field state.⁵² Since the $[Ru(tpy)_2]^{2+}$ complexes in the Ru-based CPs are covalently bound in the coordination network and not soluble in common solvents, this polymer is a permanently luminescent porous network that could be used as a robust photosensitizer in many applications.³⁴

While our terpyridine-based CPs do not adsorb N₂, they readily uptake CO₂ with surface areas ranging from 260 to 690 m² g⁻¹ (Table 1, Figs. S15–18 in ESI[†]), as determined by non-local density functional theory (NLDFT) analysis, previously shown to be an effective method for determining the surface area of microporous polymers.^{53,54} Assuming a non-interpenetrating network, the idealized diamond-cubic structure of CPs (Scheme 1) would have a 29.6 Å distance between the tetrahedral carbon nodes and surface areas that are several times larger than the aforementioned values. Thus, we believe that the CPs reported herein are highly catenated, as observed in other diamond-type structures.^{25,55,56} Indeed, density measurements (see ESI†) yield values that are much higher than expected for a non-catenated material. While such catenation unfortunately reduces the porosity of our terpyridine-based CPs, the availability of micropores, through the use of the 3D-directing monomer 4, distinguishes these materials from the nanoparticulate amorphous coordination polymers previously reported.46

Conclusions

We have synthesized a new type of hybrid porous material utilizing a rigid tetrahedral tetrakis(terpyridine) molecule as an organic node in combination with a variety of metal ions as inorganic linkers. This strategy brings terpyridine coordination complexes into the macroscopic materials arena where their photophysical/electrochemical properties are directly integrated into microporous networks. For example, the Ru(tpy)₂-based CP shown herein is a room-temperature luminescent porous material that can potentially be used in photosensitizer applications in the presence of guest molecules. While the surface areas of these materials are still modest due to catenation, the extension of the one-step ligand-directed assembly strategy to incorporate 3D-directing monomers holds much promise for engendering the micropores in amorphous CPs with the plethora of functionalities available to metal complexes.

Acknowledgements

Financial support for this work is provided by the NSF (grant # EEC-0647560 through the NSEC program), the AFOSR (grant # FA-9550-07-1-0534), and DTRA (grant # HDTRA1-09-1-0007). Partial support for the photophysical work is provided by the DOE (grant DE-FG-87ER13808). O.C.C. is an NSF-ACC Fellow (grant # CHE-0936924). We thank Mr. Brad Hauser for his help with the adsorption-desorption measurements, Dr. Jennifer L. Seymour for HRMS analysis of 4, Dr. Abraham Shultz for ICP-OES analysis, Prof. A. Ozgur Yazaydin for helpful discussion, and Ms. Dan Zheng for the luminescent optical images. We are grateful to the reviewers of this manuscript for comments that greatly strengthen our discussion.

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