Syntheses and Investigations of Photo and Radioluminescent Stilbene- and Anthracene-Based Lanthanide Metal-Organic Frameworks

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ABSTRACT

CHEMISTRY

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SYNTHESES AND INVESTIGATIONS OF PHOTO AND RADIOLUMINESCENT STILBENE- AND ANTHRACENE-BASED LANTHANIDE METAL-ORGANIC FRAMEWORKS

Committee Chair: Conrad Ingram, Ph.D.

Dissertation dated May 2016

This research explores the synthesis of anthracene and stilbene-based metal-organic framework (MOF) structures as potential scintillating (radioluminescent) materials for use in the detection of gamma radiation. The organic molecules 9,10-anthracenedicarboxylic acid (ADCH₂) and trans-4,4’-stilbenedicarboxylic acid (SDCH₂), were each used as a linker, in combination with a range of lanthanide metal ions, to synthesize novel three dimensional MOF structures under hydrothermal conditions.

With ADCH₂, the early period lanthanides yield isostructures with the metal ion in higher coordination (nine) than for those with late period metals (seven). The ADC-MOFs show linker-based photoluminescence properties with well defined vibronic peaks
in their emission profile and their emission ($\lambda_{\text{max}} \sim 435$ nm) blue shifting from that of the ADCH$_2$ powder ($\sim 500$ nm) and closer to the organic molecule in monomer arrangement ($\lambda_{\text{max}} \sim 420$ nm). The structures also show photoluminescence lifetimes between 1 and 2 ns, which is similar to the reported value for monomeric anthracene units. The blue-shift and reduction in lifetime, compared to ADCH$_2$, are indicative of minimal $\pi$-$\pi$ interactions amongst the aromatic moieties, thereby limiting the non-radiative relaxation pathways. On exposure to ionizing radiation (protons and $\gamma$-rays), the ADC-MOFs demonstrated scintillation properties, with a radioluminescence lifetime of ~ 6 ns which is similar to that of the ADCH$_2$ powder.

A combination of SDCH$_2$ and lanthanide metal ions produced two isostructured MOFs containing Tm$^{3+}$ and Er$^{3+}$, under the hydrothermal synthesis conditions explored. The 3-D structure contained ultra large diamond-shaped pores with dimensions of 16 Å x 30 Å. A blue-shift of fluorescence spectra was observed for the SDC-MOF structures ($\lambda_{\text{max}} \sim 425$ nm) compared to that of bulk SDCH$_2$ powder ($\lambda_{\text{max}} \sim 475$ nm), and closely resembling that of monomeric isolated SDC units ($\lambda_{\text{max}} \sim 475$ nm). Their photoluminescence lifetime is ~0.76 ns, about half of that observed for SDCH$_2$ powder. The blue shift and reduction in lifetime (compared to SDCH$_2$) is attributed to minimal $\pi$-$\pi$ interactions between SDC units in the MOF structure, thus minimizing associated non-radiative relaxation pathways.

The isolation of anthracene and stilbene in MOF structures therefore has the potential to improve their performance as scintillators.
SYNTHESES AND INVESTIGATIONS OF PHOTO AND RADIOLUMINESCENT
STILBENE- AND ANTHRACENE-BASED LANTHANIDE METAL-ORGANIC
FRAMEWORKS

A DISSERTATION
SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY
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THE DEGREE OF DOCTOR OF PHILOSOPHY

BY
STEPHAN ROY MATHIS, II

DEPARTMENT OF CHEMISTRY

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<th>Abbreviation</th>
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<tr>
<td>ADC</td>
<td>9,10-anthracenedicarboxylate</td>
</tr>
<tr>
<td>ADC-Na</td>
<td>9,10-anthracenedicarboxylate sodium salt</td>
</tr>
<tr>
<td>ADCH₂</td>
<td>9,10-anthracenedicarboxylic acid</td>
</tr>
<tr>
<td>CP</td>
<td>Coordination polymer</td>
</tr>
<tr>
<td>DEF</td>
<td>N’N-diethylformamide</td>
</tr>
<tr>
<td>DMF</td>
<td>N’N-dimethylformamide</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Analysis</td>
</tr>
<tr>
<td>IBIL</td>
<td>Ion-beam induced luminescence</td>
</tr>
<tr>
<td>Iπ</td>
<td>π-electron ionization</td>
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<tr>
<td>Ln</td>
<td>Lanthanide</td>
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<tr>
<td>MOFs</td>
<td>Metal-Organic Frameworks</td>
</tr>
<tr>
<td>PBET</td>
<td>Proton Beam Exposure Time</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PMTs</td>
<td>Photomultiplier tubes</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powdered X-ray diffraction</td>
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<td>QE</td>
<td>Quantum Efficiency</td>
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<tr>
<td>RL</td>
<td>Radioluminescence</td>
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<tr>
<td>SBU</td>
<td>Secondary building units</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SCXA</td>
<td>Single Crystal X-ray Analysis</td>
</tr>
<tr>
<td>SDC</td>
<td>4,4’-stilbenedicarboxylate</td>
</tr>
<tr>
<td>SDC-Na</td>
<td>4,4’-stilbenedicarboxylate sodium salt</td>
</tr>
<tr>
<td>SDCH₂</td>
<td>4,4’-stilbenedicarboxylic acid</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TCSPC</td>
<td>Time correlated single photon counting</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>VDPs</td>
<td>Voronoi Dirichlet Polyhedrals</td>
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CHAPTER I
INTRODUCTION

The need for advances in the science of detection of radiation from subatomic particles (protons, neutrons, and gamma radiation) is of significant importance in radiography, biological safety, and nuclear material identification and monitoring.¹ The development of more efficient detectors for gamma radiation generated by fissile materials is of particular interest. This research explores the synthesis of metal-organic framework (MOF) structures as potential scintillating (radioluminescent) materials for use in the detection of gamma radiation.

Current radiation detectors are based mainly on scintillators. The performance of these scintillators is affected by several factors, including interspecies interactions, atomic density, chemical composition, and crystal symmetry. Current material types, such as inorganic scintillating molecules, offer little flexibility in design.

Organic scintillators, such as naphthalene, anthracene, and stilbene, have the ability to discriminate between subatomic particles and gamma rays, since the delayed fluorescence they produce depends on the nature of these exciting particles. These scintillators, with scintillation based on energy transitions due to excitable electrons in the π-bonds, exhibit fast luminescence lifetimes and high light intensity. However, they have low crystal density and are difficult to grow into large size crystals, which limits their applications in radiation detection. Their low density and small cross sections

¹
adversely affect their mass stopping power for the gamma radiation.\textsuperscript{1,2} The drawbacks of the organic scintillators may be overcome by creating dense structures, but with adequate spacing between the organic scintillating molecules to isolate them and enhance their luminescent properties. The isolation of the organic chromophore can minimize the organic scintillator’s ability to undergo dimerization under irradiation, reduce non-radiative relaxation pathways, and increase quantum yield. The isolation of the chromophore may be achieved by utilizing the respective organic molecule to construct multidimensional MOF structures.

MOFs are multidimensional crystalline coordination polymer (CP) materials that are created by the coordination of metal ions and electron donating organic molecules through functional groups such as amines or carboxylates. The presence of both organic and inorganic components enables both the pore size and chemical environment of the MOFs’ structures to be controlled.

In this investigation, the syntheses of MOFs containing anthracene and stilbene as ligand backbones were explored. The lanthanide ions were used as the metal ions since they have a high propensity for large coordination numbers, ranging between six to nine. Therefore, their potential to promote a wide variety of 3-D connectivity and to effectively isolate the organic molecules was envisioned. Herein, the synthesis of new lanthanide MOFs that possess stilbene and anthracene ligands and the investigation of their scintillation properties are presented.

Chapter II presents a literature review of scintillation technologies. This chapter also presents a review of MOF’s synthesis and their linker-based fluorescence and
scintillation properties.

Chapter III describes the structures of new isostructural scintillating MOFs that were synthesized with the early period lanthanide ions, \((\text{Sm}^{3+}, \text{Eu}^{3+} \text{ and } \text{Tb}^{3+})\) and 9,10-anthracenedicarboxylate (ADC) ligand. The chapter also explores the role of the 3-D arrangements in allowing ADC ligands to be effectively separated so as to promote photoluminescence and radioluminescence with little or no interchromophore coupling.

Chapter IV describes the synthesis and structure of new isostructural scintillating MOFs based on ADC and late period lanthanide ions, (namely, \(\text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}\) and \(\text{Yb}^{3+}\)). This chapter highlights differences in the crystal structure than the MOFs described in Chapter III. The chapter highlights that these structures are more densely packed, but with chromophore spacing remaining large enough to exhibit monomeric chromophore luminescence features.

Chapter V reports the synthesis of a unique set of isostructural MOFs comprised of \(\text{trans-}4,4’\)-stilbenedicarboxylate (SDC) and \(\text{Tm}^{3+}\) and \(\text{Er}^{3+}\) as lanthanide ions. The crystal structures exhibit unit cells with large diamond-shaped pores. In these low density structures, the SDC units are locked in place and prevents \(\text{cis-trans}\) isomerization of the ligand as a result. The chromophore spacing was large enough to reduce interchromophore coupling and decrease non-radiative pathways during luminescent emission.
2.1 Scintillation

Scintillation is a form of luminescence whereby light is emitted after ionizing radiation is absorbed by a material. The interaction with ionizing radiation leads to $\pi$-electron ionization ($\text{I}_{\pi}$) followed by ion recombination (the recombining of secondary electrons with their parent positive ion) that populates available singlet and triplet states (Figure 2.1).$^{3,6}$ This is then followed by non-radiative thermal deactivation to the lowest vibrational level of the first excited state, $S_{1,0}$, followed by luminescence. A series of singlet states are labeled as $S_{0}$, $S_{1}$, $S_{2}$, ..., and triplet states are labeled as $T_{1}$, $T_{2}$, $T_{3}$, .... The energetic gap between the ground state and the first excited state is approximately 3 to 4 eV for organic molecules.$^{2}$ Each energy level contains various vibrational levels. Typical spacing of the vibronic levels for organic molecules is on the order of 0.15 eV.$^{2}$
In scintillation, the transition processes involve absorption of kinetic energy from a charged particle nearby. Radiationless internal conversion is responsible for the de-excitation to the $S_1$ electron state. States with excess vibrational energy will then quickly lose that vibrational energy. The net effect of the excitation process produces excited molecules in the first excited state.$^2$

The principal scintillation light is emitted in transitions between the $S_1$ excited state and one of the vibrational levels of the ground electronic state. The decay lifetime can be calculated from the first excited state, and the fluorescence intensity at a time $t$ following excitation can be determined by Equation 1:
where $\tau$ is the fluorescent decay time, $I$ is the fluorescence intensity, and $I_0$ is the prompt fluorescence intensity due to fast singlet state transitions. In most organic scintillators, the fluorescence decay time is only a few nanoseconds.\textsuperscript{2}

The lifetimes for the first triplet state transitions in both fluorescence and scintillation are characteristically much longer than that of the singlet state, $S_i$. Intersystem crossing can convert some singlet states into triplet states. The lifetime, $T_i$, may be as much as $10^{-3}$ seconds, and the radiation emitted from $T_i$ to $S_0$ is delayed light emission characterized as phosphorescence. Since $T_i$ is lower in energy than $S_i$, the emission $\lambda$ will be longer than that observed in fluorescence. However, $T_i$ can be excited back into the $S_i$ state and subsequently decay through normal fluorescence. This is the process for the delayed fluorescence in organic molecules.\textsuperscript{2}

Organic scintillators are generally used for the detection of beta particles (fast electrons) and alpha particles.\textsuperscript{7} Scintillators of this nature have small cross-sections for gamma rays, which lowers the throughput of radiation detection. Scintillators, such as naphthalene, anthracene, and stilbene, exhibit fast luminescent lifetimes and high light intensity. However, these organic scintillators are not widely used because of difficulty in growing large crystals and the fragility of the crystals.

Anthracene, which consists of three fused benzene rings, exhibits blue fluorescence in dilute solution and yellow fluorescence as a powder. Anthracene has the highest light output among known organic scintillators.\textsuperscript{2} However, this organic molecule is difficult to grow as large crystals and the crystals are fragile in a bulk solid.
Furthermore, the orientation of an ionizing particle with respect to the crystal axis can impact scintillation efficiency, and the natural arrangement of anthracene in a bulk solid is not conducive to high scintillation efficiency.\(^8\) Anthracene also dimerizes when exposed to UV radiation, which inhibits its ability to resist radiation damage (Figure 2.2a).\(^9\)

Stilbene is well documented as a fluorescent molecule.\(^{10-12}\) Stilbene is used as an optical brightener, phosphor, scintillator, and as a dye. Stilbene undergoes \(\pi \rightarrow \pi^*\) electron excitation by absorption of UV light at wavelength in the 330 nm region.\(^{13}\) As a free-standing monomer, stilbene undergoes \textit{cis-trans} isomerization under UV irradiation, which results in a loss of radiative light emission. The radiation energy that would be used in the absorption-emission processes instead is used to change conformations, and its fluorescence efficiency is reduced as result. Though it has a lower scintillation efficiency than anthracene, stilbene is still of adequate sufficiency to be utilized in scintillator devices.\(^{13-21}\)

Inorganic scintillator materials are a separate class of scintillators. Their inability to maintain luminescence at room temperature is a major challenge for their application. None provide the desired combination of stopping power, light output, or decay time. They are lacking in the ability to be both bright and fast.\(^{22}\) PbI\(_2\), for example, is a scintillator with fast scintillating lifetimes at cryogenic temperatures, but its luminosity decreases with increasing temperature.

Plastic scintillators are a combination of a fluorescent emitter suspended in a base. The base is comprised of a solid polymer matrix. Polyethylene naphthalate as a
polymeric plastic scintillator, is used without additives and is expected to replace existing plastic scintillators due to its high performance. However, plastic scintillators are known to show light output saturation at high energy densities and have low tolerance for radiation damage.

In this research, we explored the incorporation of anthracene and stilbene as the linker in MOF structures in order to improve their performance as scintillators. These organic molecules will provide the bulk of mass for the MOFs and are expected to be the predominant source of luminescence in the structures.

The orientation of the linker plays a large part in linker-based luminescence, and the isolation of the ligands are important in decreasing the non-radiative pathways during ligand emission. This reduction of non-radiative pathways is often accompanied by faster fluorescence lifetimes and quantum yields. Therefore, incorporating anthracene as its dicarboxylate derivative into a MOF eliminates the disorientation that would otherwise be present in multiple ADC units packed in the bulk solid of the organic molecule, thereby decreasing the probability of non-radiative relaxation pathways (Figure 2.2b).
Figure 2.2. a) Dimerization of anthracene in solution, and b) 9,10-anthracenedicarboxylic acid.\(^9\)

Using anthracene as the linker component of MOFs is proposed to yield a robust structure because of the ligands’ inability to dimerize, based on the fixed distance between the ligands under standard conditions. MOF structures also offer the ability to lock stilbene in the trans configuration after irradiation. The trans configuration allows for greater efficiency in radiative emissions after irradiation. Trans-4,4’-stilbenedicarboxylic acid (SDCH\(_2\)) (Figure 2.3a) has been proven to be an effective ligand in coordination polymers.\(^{10-13}\) Cis-4,4’-stilbenedicarboxylic acid occurs from SDCH\(_2\) after irradiation in solution and exhibits limited fluorescence (Figure 2.3b).
Figure 2.3. a) trans-4,4’-stilbenedicarboxylic acid and b) and cis-4,4’-stilbenedicarboxylic acid.

2.2 MOFs

MOFs are crystalline 2-D and 3-D coordination polymer materials whose structures are created by forming coordination bonds between metal ions (Lewis acid) and electron donating molecules such as amides or carboxylates (Lewis base). In many instances, the structures contain voids, channels and pores, and the presence of both organic and inorganic components enable both the pore size and chemical environment to be tunable.26
2.2.1 MOF Properties

The luminescence behavior of MOFs is dependent on the structure and intermolecular packing. Fluorescence and phosphorescence exist as basic forms of luminescence. These two emission pathways are due to the multiple spin states during the radiative relaxation process.\textsuperscript{27}

There are four ways in which MOFs demonstrate luminescence: 1) Linker-based luminescence, 2) metal-based luminescence, 3) charge transfer between organic and inorganic species and, 4) guest molecules in the MOF structure (Figure 2.4).\textsuperscript{28-30} Linker-based luminescence, the focus of this research, is described below.

Figure 2.4. Schematic of typical emission pathways in MOFs.\textsuperscript{25}

The nature of linker-based luminescence in MOFs is determined by four main factors, namely: 1) the conjugation of the linker, 2) energy difference between the linker triplet state and the resonant emissive lanthanide energy level, 3) the orientation of the
linkers and its degree of isolation through the coordination geometry, and 4) the atomic radii of the metal.$^{25,30}$

MOFs can incorporate a large range of π-conjugated organic molecules. The fluorescent emission from organic linkers corresponds to the emission transition from the lowest excited singlet state to the singlet ground state, and the transitions are either $\pi^* \rightarrow \pi$ or $\pi \rightarrow n$ in nature. The metal ion can affect the luminescence behavior of the organic linkers as they can regulate the intermolecular distances, and hence the intermolecular and intramolecular interactions amongst the organic linkers.$^{30-32}$

Fluorophores are fluorescent chemicals that can re-emit light upon excitation. They typically contain π-bond conjugated molecules, and frequently include aromatic groups. The main features of fluorophores that are of interest in scintillation are high quantum yield, short lifetime, low extinction coefficients, excitation, emission wavelength, and Stokes shift. A wide range of fluorescent organic linkers have been used in MOFs, common examples of which are listed in Table 2.1.
Table 2.1. Examples of fluorophores used in MOFs

<table>
<thead>
<tr>
<th>Ligand Name</th>
<th>Structure</th>
<th>Luminescence</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Trans</em>-4,4′-stilbenedicarboxylic acid</td>
<td><img src="image1" alt="Structure" /></td>
<td>Linker-based, sensing, scintillation</td>
</tr>
<tr>
<td>1,3,5-Benznetricarboxylic acid</td>
<td><img src="image2" alt="Structure" /></td>
<td>Linker-based, Ln-antenna</td>
</tr>
<tr>
<td>2,6-Anthracene dicarboxylic acid</td>
<td><img src="image3" alt="Structure" /></td>
<td>Linker-based, excimer</td>
</tr>
</tbody>
</table>

Stilbene and anthracene based ligands are known to exhibit linker-based luminescence, which makes them good candidates for scintillating MOFs.

In general, when an organic molecule absorbs a photon, chains of photophysical events occur. These events include vibrational relaxation, intersystem crossing, phosphorescence and fluorescence. Fluorescence of organic molecules corresponds to the energy transition from the singlet state $S_1$ to the ground state $S_0$. The transition between $S_1 \rightarrow S_0$ is molecular fluorescence, which is spin allowed and has a lifetime of approximately 10 to 1000 ns. Phosphorescence, on the other hand, refers to radiative transitions from the triplet state $T_1$ to $S_0$, which is spin forbidden and has a lifetime as long as 100 seconds (Table 2.2).
Table 2.2. Observed electronic transitions in fluorescent lifetime measurements

<table>
<thead>
<tr>
<th>Process</th>
<th>Transition</th>
<th>Timescale (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Absorption</td>
<td>( S_0 \to S_n )</td>
<td>ca. 10^{-15}</td>
</tr>
<tr>
<td>Internal Conversion</td>
<td>( S_n \to S_1 )</td>
<td>10^{-14} to 10^{-11}</td>
</tr>
<tr>
<td>Vibrational Relaxation</td>
<td>( S_n^* \to S_n )</td>
<td>10^{-12} to 10^{-10}</td>
</tr>
<tr>
<td>Intersystem Crossing</td>
<td>( S_1 \to T_1 )</td>
<td>10^{-11} to 10^{-6}</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>( S_1 \to S_0 )</td>
<td>10^{-9} to 10^{-6}</td>
</tr>
<tr>
<td>Phosphorescence</td>
<td>( T_1 \to S_0 )</td>
<td>10^{-3} to 100</td>
</tr>
<tr>
<td>Non-Radiative Decay</td>
<td>( S_1 \to S_0 )</td>
<td>10^{-7} to 10^{-5}</td>
</tr>
</tbody>
</table>

2.2.2 Anthracene and Stilbene based MOFs

Anthracene and stilbene MOFs are the focus of this research, therefore their presence in MOF structures is discussed below. A 3-D coordination complex based on ADC in coordination with cadmium and lanthanum ions was reported by Wang et al.\(^{34}\) The luminescence for each compound was observed at 430 and 525 nm, indicative of linker-based luminescence. The density for the Cd-ADC and La-ADC structures were 1.137 and 1.496 g/cm\(^3\), respectively. The La-ADC is the only lanthanide metal reported with ADC to date.\(^{34}\)

Cadmium- and zinc-containing 3-D MOFs with anthracene based ligands were reported by Wang et al.\(^{35}\) Two ligands, ADC and 1,5-anthracenedicarboxylic acid, were used in the MOFs. The structures exhibit luminescent emission peaks at 440, 485, and 525 nm which were attributed to the organic linkers. Wang et al. also reported a 3-D zinc
coordination polymer based on ADC and 9-anthracene carboxylic acid.\textsuperscript{36} The coordination polymer exhibited linker-based luminescence properties with an emission peak around 490 nm. Liu et al. reported a luminescent 3-D silver coordination polymer with ADC and hexamethylenetetramine, that exhibits linker-based luminescence at 440 nm.\textsuperscript{37} Liu et al. also reported a 3-D cadmium coordination polymer based on ADC in combination with 2,2’-bipyridyl-like chelating ligand that exhibit linker-based luminescence at 440 nm.\textsuperscript{38}

Other reports of ADC based MOFs that were synthesized, but for which no luminescence studies were presented, are highlighted below. Kojtari et al. reported a 3-D MOF with ADC and zinc that has a packing density of 1.733 g/cm\textsuperscript{3}.\textsuperscript{39} Chen et al. reported an ADC based magnesium coordination polymer with a density of 1.401 g/cm\textsuperscript{3}.\textsuperscript{40} Ma et al. reported a 2-D nanotubular ADC based Ni-MOF, with a density of 1.007 g/cm\textsuperscript{3}.\textsuperscript{41} Ma et al. also reported a 3-D ultramicroporous ADC based Zn-MOF, with a density of 1.245 g/cm\textsuperscript{3}.\textsuperscript{42} Mu et al. combined ADC ligand with 1,4-naphthalene dicarboxylic acid and 1,5-bis(imidazole)pentane and cobalt to synthesize a coordination polymer with a packing density of 1.611 g/cm\textsuperscript{3}.\textsuperscript{43}

There have also been several reports of stilbene based MOFs. Bauer et al.\textsuperscript{44} reported two MOFs based on the combination of SDC ligand with zinc. One of the frameworks is a 2-D structure, with a density of 1.524 g/cm\textsuperscript{3}. The other is an interpenetrating 3-D structure with a density of 0.503 g/cm\textsuperscript{3}. Both show linker-based luminescence with emission maximums at 441 nm and 390 nm, respectively. The difference in the peak positions between the MOFs were attributed to interligand spacing.
Further, the fluorescence lifetimes were shorter for the MOFs than for the SDCH$_2$ bulk powder. Doty et al. investigated scintillating properties of the two stilbene based MOFs above using ion beam induced luminescence spectroscopy and both showed Stokes shifts between their excitation and emission spectra.\(^7\)

A series of SDC based 3-D MOFs with ions of five lanthanide metals (samarium, europium, gadolinium, terbium and erbium), each with a different crystal structure, were reported by Deng et al.\(^{45}\) Their densities ranged from 1.845 to 2.082 g/cm\(^3\), which are amongst the highest densities reported for lanthanide metal based SDC MOFs.

Huang et al.\(^{46}\) reported a cadmium-SDC 3-D MOF that exhibited linker-based luminescence with an emission maximum at 460 nm. Xiao et al.\(^{47}\) reported a photoluminescent 3-D pillared layer structure synthesized with zinc, SDC, and 1,2,4-triazole, with linker-based luminescence at 443 nm. A series of layered and pillared 3-D MOF made with zinc, 1,2-bis(4-pyridyl)ethane, and SDC were reported by Cheng et al.\(^{48}\) These structures possess a range of packing densities between 1.347 to 1.530 g/cm\(^3\), and exhibited linker-based luminescent peaks at 460, 487, and 469 nm.

Liu et al.\(^{15}\) reported that the combination of 1,4-bis(2-methyl-imidazol-1-yl)butane and SDC created a MOF structure with a density of 1.392 g/cm\(^3\). A 2-D coordination polymer with 2 nm channels, based on SDC and aluminum was reported by Liu et al.\(^{13}\) Wang et al.\(^{49}\) reported 3-D interpenetrated framework assemblies based on SDC and zinc, cadmium, and nickel. Ma et al.\(^{50}\) reported 1-D, 2-D, and 3-D coordination polymers from SDC with copper, cadmium, cobalt, and nickel. The densities of the Cu-SDC, Cd-SDC, Co-SDC, and Ni-SDC MOFs ranged from 1.33 to 1.46 g/cm\(^3\). Plater et
al.\textsuperscript{51} reported that SDC combined with cobalt and 2,2'-bipyridyl crystallized into coordination polymers with a unit cell volume of 2213.45 Å\textsuperscript{3}.

\subsection{2.2.3 Scintillating MOFs}

Scintillating MOFs have only been reported in a few studies. There are four levels of structural complexity that affect scintillation and luminescence efficacy in a MOF.\textsuperscript{52} The first level is called the primary structure, which involves the organic ligands, metals and their coordination sphere. The second level is the framework interpenetration and other linker interactions beyond the immediate sphere of coordination. The third level is the tertiary structure, which encompasses framework dynamics and structural flexibility. The final level is a quaternary structure, which is the interaction of the framework with guest molecules. We will be focusing on the primary and secondary levels to achieve luminescence efficacy.

Doty et al.\textsuperscript{7} reported the first studies on scintillating MOFs. The structure was made from SDC and zinc, as highlighted earlier. Ion beam induced luminescence (IBIL) spectroscopy was used to investigate the scintillation properties of the SDC based zinc MOFs. The studies showed that the SDC-MOFs exhibited radiation damage resistance.

As a follow up to the above studies, Feng et al. further investigated the scintillation properties of some previously reported 3-D MOF structures.\textsuperscript{53} By probing scintillation using IBIL, it was found that IRMOF-10 (Zn-4,4'-biphenyldicarboxylic acid), IR-MOF-8 (Zn-2,6-naphthalenedicarboxylic acid), and two MOFs with Al-2,6-napthalenedicarboxylic acid all luminesce under irradiation.
Cathodoluminescence, which is based on an electron beam as the source of ionizing radiation, was used to probe the radioluminescence of NOTT-103-Zn (5,5’-(naphthalene-2,6-diyl)diisophthalic acid; zinc), PCN-14-Zn (5,5’-(anthracene-9,10-diyl)diisophthalic acid; zinc), and DUT-6 (benzene-1,3,5-trisbenzoate, 2,6-naphthalenedicarboxylic acid; zinc). Small Stokes shifts during cathodoluminescence were observed for these MOFs, which demonstrated that they were fairly resistant to radiation damage.\textsuperscript{36}

In summary, the scintillation properties of MOFs and their potential application as scintillators for radiation detection have been demonstrated for only a few SDC-based structures with d\textsuperscript{10} transitional metals, namely Zn\textsuperscript{2+} and Cd\textsuperscript{2+} SDC. Transition metals with a d\textsuperscript{10} valence shell are extensively used because their filled orbitals allow them to have little or no influence on the ligand emission properties.

As an alternative to the transition metals, lanthanide ions are large and have a high propensity for 3-D connectivity in MOFs, which is widely known. However, their use as metal ions to effectively isolate the organic molecules, namely stilbene and anthracene, in MOFs is envisioned and has not been previously explored. The synthesis of scintillating MOFs containing Ln ions, anthracene, and stilbene was therefore explored in this work.
CHAPTER III
SYNTHESIS AND PHOTO- RADIOLUMINESCENCE INVESTIGATIONS OF MOFS
FROM ANTHRACENE AND EARLY PERIOD LANTHANIDE IONS

3.0 Introduction

The syntheses of MOFs using ADCH₂ and the early period lanthanide metals of large atomic radii, namely, cerium through terbium, were explored. During synthesis, the metal:ligand ratio was generally 2:1. The solvents investigated included N’N-diethylformamide (DEF) and N’N-dimethylformamide (DMF)/H₂O (1:1), temperature ranged from 85 to 105 °C, and the progress of crystallization was monitored daily by visual observation of the synthesis vial. The photo- and radioluminescence characteristics of the resulting MOFs were then investigated.

3.1 Experimental Method

**Compound 1** (C₆₃H₅₉N₅O₁₇Sm₂): A mixture of Sm(NO₃)₃•6 H₂O (0.1 mmol, 0.044 g), ADCH₂ (0.05 mmol, 0.013 g) and DMF/H₂O (10 mL/ 10 mL) was sealed in a 20 mL scintillation vial and heated to 105 °C for 72 h in a convection oven. The vial was allowed to cool to room temperature and the colorless crystals were filtered and repeatedly washed with fresh DMF at room temperature along with vacuum filtration. (Yield = 79%, 0.012 g, based on ADCH₂). Elemental Anal. (%) C, 51.88; H, 4.20; N,
4.64. Calcd. (％) C, 51.89; H, 4.05; N, 4.80. IR (KBr pellet, cm⁻¹): 3341br, 1562s, 1450m, 1327s, 1284m, 1176w, 1105w, 1029w, 839s, 794m, 736m, 686s, 600w, 468m.

**Compound 2** (C₆₃H₅₉N₅O₁₇Eu₂): The synthesis procedure was similar to **Compound 1**, except, Eu(NO₃)₃•6 H₂O was used as lanthanide metal salt (0.1 mmol, 0.043 g). The vial was allowed to cool to room temperature and the colorless crystals were filtered and repeatedly washed with fresh DMF at room temperature along with vacuum filtration. (Yield = 72%, 0.011 g, based on ADCH₂). Elemental Anal. (％) C, 51.80; H, 4.17; N, 4.92. Calcd. (％) C, 51.77; H, 4.04; N, 4.79. IR (KBr pellet, cm⁻¹): 3341br, 1562s, 1450m, 1327s, 1284m, 1176w, 1105w, 1029w, 839s, 794m, 736m, 686s, 600w, 468m.

**Compound 3** (C₆₃H₅₉N₅O₁₇Tb₂): The synthesis procedure was similar to **Compound 1**, except, Tb(NO₃)₃•6 H₂O was used as lanthanide metal salt (0.1 mmol, 0.045 g). The vial was allowed to cool to room temperature and the colorless crystals were filtered and repeatedly washed with fresh DMF at room temperature along with vacuum filtration. (Yield = 72%, 0.011 g, based on ADCH₂). Elemental Anal. (％) C, 51.22; H, 4.04; N, 4.80. Calcd. (％) C, 51.27; H, 3.99; N, 4.74. IR (KBr pellet, cm⁻¹): 3341br, 1562s, 1450m, 1327s, 1284m, 1176w, 1105w, 1029w, 839s, 794m, 736m, 686s, 600w, 468m.

**Nd-ADC** (C₆₃H₅₉N₅O₁₇Nd₂): The synthesis procedure was similar to **Compound 1**, except, Nd(NO₃)₃•6 H₂O was used as lanthanide metal salt (0.1 mmol, 0.044 g). The vial was allowed to cool to room temperature and the colorless crystals were filtered and repeatedly washed with fresh DMF at room temperature along with vacuum filtration. (Yield = 72%, 0.011 g, based on ADCH₂).
**Gd-ADC** (C_{60}H_{58}N_{4}O_{19}Gd_{2}): Synthesis procedure similar to **Compound 1**, except Gd(NO_3)_3•6 H_2O was used as lanthanide metal (0.045 g). The vial was allowed to cool to room temperature and the colorless crystals were filtered and repeatedly washed with fresh DMF at room temperature along with vacuum filtration. (Yield = 79%, 0.012 g, based on ADCH_2). Elemental Anal.(%) C, 45.75; H, 3.71; N, 3.39. Calcd (%) C, 48.51; H, 3.90; N, 3.77.

### 3.1.1 Structure Analysis using X-ray diffraction

X-Ray diffraction is based on the principle of Bragg’s Law.\(^{54}\) Bragg’s Law is:

\[
n\lambda = 2d \sin \theta \quad \text{Equation 2}
\]

where \(n\) is the order, \(\lambda\) is the X-ray wavelength, \(d\) is the spacing between lattice planes, and \(\theta\) is the incident or diffracted beam and the diffraction planes. The wavelength of the X-ray used in diffraction experiments range from 0.5 to 2.5 Å. The beam is on the order of interatomic distances, and can irradiate a material to create a diffraction pattern. If the sample is crystalline, the diffraction pattern is in reciprocal space of an ordered atomic structure. The three dimensional arrangement of the atoms in the direct space is then interpreted. From this data, it is possible to refine and solve crystal structures of materials.\(^{54}\)

### 3.1.2 Single Crystal X-ray Analysis

Single crystal X-ray analysis (SCXA) requires unfractured and optically clear single crystals. Usually, monochromatic Mo K\(\alpha\) radiation (\(\lambda = 0.7108\) Å) or Cu K\(\alpha\) (\(\lambda =
1.5418 Å) is used and the diffractometer is equipped with a 2-D image plate detector.\textsuperscript{54} From the solved structure, bond lengths, bond angles, torsion angles, π-stacking, and hydrogen bonds are provided.

For SCXA, a suitable crystal was isolated and mounted onto the instrument using Paratone Oil on a Bruker APEX-II CCD diffractometer. A Mo Kα radiation of 0.71073 Å wavelength was used to analyze the crystal at 110 K with an Oxford cryostream low-temperature apparatus during data collection. Numerous reflections were collected and subjected to refinement. Measurements were made at ω scans of 1° per frame for 40s using Mo Kα radiation (fine-focus sealed tube, 45 kV, 30 mA). The structure was solved with the Superflip structure solution program, using the Charge Flipping solution method\textsuperscript{29} and using Olex2 as the graphical interface. The model was refined with version 2013-4 of ShelXL using Least Squares minimization.\textsuperscript{57} The total number of runs and images was based on the strategy calculation from the program APEX2.\textsuperscript{58} Cell parameters were retrieved using the SAINT\textsuperscript{59} software and refined using SAINT\textsuperscript{59}. Data reduction was performed using the SAINT\textsuperscript{59} software which corrects for Lorentz polarization. All non-hydrogen atoms were refined anisotropically. Hydrogens positions were calculated geometrically and refined using the riding model.\textsuperscript{60}

### 3.1.3 Powder X-ray Diffraction

Powdered samples were mounted onto a Panalytical Empyrean Series 2 X-ray diffractometer. The X-ray source was a Cu Kα (\(λ = 1.5418\text{ Å}\)) anode, and diffraction patterns were obtained between the 2θ angles of 4° - 40°, with a step size of 0.026° and dwell time of 147.5 seconds. The Cu anode material was used at a voltage of 45 kV and
current of 40 mA. The sample holder was mounted in the path of the X-ray beam. The Panalytical X’Pert Data Viewer software was used to analyze diffraction patterns. Simulated PXRD patterns were obtained from SCXA data using Mercury 3.1 software from Cambridge Crystal Structure Database.54

3.1.4 Fourier Transform Infrared Analysis

Fourier transform infrared analysis (FTIR) includes the absorption, reflection, photoacoustic, or emission spectrum obtained from an optical interferogram. The importance of this method is that it can measure many vibrational frequencies simultaneously. The real advantage of an FTIR spectrometer is obtained through the presence of an interferometer rather than a grating or prism, as in conventional spectrometers.

IR spectra were collected using a Bruker Alpha-P FTIR spectrophotometer. Samples were prepared as KBr pellets and their spectra were obtained between 4000 to 350 cm\(^{-1}\), with fourteen cumulative scans. Background spectrum was collected and subtracted from each sample spectrum.

3.1.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) records changes in weight as a function of increasing temperature. The basic instrumental requirements for TGA are a precision balance and a furnace that is programmed for a linear rise of temperature with time. TGA results can be presented as weight versus temperature (TGA curve), and/or rate of weight change versus temperature curve (differential TGA curve).62
Thermal analysis was conducted on a TA Instrument Q50 thermal analyzer. The temperature range monitored was between 25 to 900 °C with a heating rate of 10 °C/min in air or nitrogen. The processing of the data was conducted using the TA Instrument thermal analyzer software.

3.1.6 Solid State Fluorescence Measurements

Fluorescence is the emission of light by a substance that has absorbed electromagnetic radiation. In most cases, the emitted wavelength is longer than that of the absorbed radiation.

Solid state emission spectra were obtained at ambient temperature on a Horiba SPEX Fluorolog 3 spectrophotometer that was equipped with a xenon lamp as a source of excitation light. The instrument was also equipped with a fluorescence lifetime measurement apparatus and quantum efficiency capabilities using the Horiba Quanta-Phi accessories. Samples were vertically mounted on a glass slide that was placed in the path of the beam. Samples in dilute solution were loaded into a standard quartz cuvette, which was then placed on a solid/aqueous interchangeable sample stage during analysis.

3.1.7 Scintillation Lifetime Measurements

Radioluminescence spectroscopy measurements were conducted using a $^{137}$Cs radioisotope source. The radioisotope source emits $\gamma$-rays which ionize the sample under investigation. Time-resolved radioluminescence decay was measured by collecting the emitted light from samples.
The longer, non-exponential time component, if observed, is based on the $\tau_s$ (delayed) and is not seen in photoluminescence (PL).\textsuperscript{52} A $^{137}$Cs source was used to produce $\gamma$ radiation (0.66 MeV, 70.1 $\mu$Ci) for this experiment.\textsuperscript{52} The setup involves two photomultiplier tubes and a light tight box originally used by Bollinger and Thomas\textsuperscript{63} and Doty et al.\textsuperscript{7} (Figure 3.1). The two photomultiplier tubes (PMTs) serve separate functions. The first PMT (Hamamatsu H5783-04) acts as a trigger, and is coupled to the sample. The second PMT (Hamamatsu H9305-03) collects photons and is equipped with an attenuator to reduce the amount of photons it receives and processed by the digital oscilloscope (Lecroy Waverunner 6200A, 2 GHz) as a delayed signal corresponding to the trigger. A small quantity of the sample was suspended between two glass coverslips with Visilox-788 optical grease, and mounted on the PMT lens. The $^{137}$Cesium source was placed very close to the sample as a continuous excitation source, but not in the way of either PMT so as to not interfere with data collection.
Figure 3.1. Diagram of time correlated single photon counting setup for scintillation lifetime measurements.\textsuperscript{3}

Intensity vs. time decay curves are fitted to the equation below (Equation 3) that has exponential and non-exponential time components.

\[ I = A_1 \exp\left(-\frac{\tau}{\tau_1}\right) + A_2 \exp\left(-\frac{\tau}{\tau_2}\right) \quad \text{Equation 3} \]

where \( I \) is the intensity, \( A \) is the numerical factor, \( \tau \) is the time, \( \tau_1 \) and \( \tau_2 \) are the lifetime factors.\textsuperscript{63} The faster linear component is attributed to prompt scintillation (\( \tau_1 \)) and usually agrees with the fluorescence decay time.
3.1.8 Ion Beam Induced Luminescence (IBIL)

High energy ion ($H^+$, $He^+$) beams can interact with materials to produce strong luminescence (IBIL) and can be used to gain information on the defect present in their structures.

IBIL provides information about the ionic state of atoms by studying the emitted photons in the UV, Visible, and IR region. The interaction of the ion beam with the atoms (or nuclei) of the target material induces from it the emission of secondary radiation. This has an energy characteristic of the emitting atom or nucleus within the material. The use of light ions such as $H^+$, $He^+$, with MeV energies allows for radiation penetration to a depth of several microns. This variation of ion species and their energies allow precise control of ionization and ion-induced damage within a material.

The proton dose to which the sample surface is exposed is determined by the equation:

$$Dose = \frac{nA}{cm^2 \times e} \times BET = cm^2$$

Equation 4

where $nA/cm^2$ is the proton beam current density, $e$ is the charge of an electron ($1.602 \times 10^{-19}$ C), and $BET$ is the beam exposure time (s).

Previous studies used high energy protons from an ion microprobe and a source of alpha particles to characterize scintillating MOFs. The proton beam simulates the production of recoil protons by the fast scattering of neutrons within the scintillator and can lead to radioluminescence (RL). The luminescence is collected by an optical fiber, dispersed by a monochromator, and detected using a charged coupled device (Figure 3.2).
The decay rates for IBIL can be determined from the following equation:

$$I = \exp \left( -\frac{D}{D_0} \right)^{\beta}$$  \hspace{1cm} \text{Equation 5}

where $I$ is the intensity (a.u.), $D$ is the dose (the amount of ions during the exposure time in $10^{15}$/cm$^2$), and $D_0$ and $\beta$ are empirical fitting constants.

Dose is the amount of ions that interact with specific area for a certain amount of time. The mass stopping power (MeV/(g/cm$^2$)) of a material depends on the nature of the material and on the radiation’s speed.

The beam spot size is the area of which the beam is interfacing with the surface of the crystal (cm$^2$). The beam current density is the current (nA) in a unit area (cm$^2$) as shown in Figure 3.2.

In the experiments reported herein, beam current densities of 472 nA/cm$^2$, 1330 nA/cm$^2$, 2700 nA/cm$^2$, and 12000 nA/cm$^2$ were used to induce samples at a
1.5 MeV and 2.5 MeV beam energy. The samples were first evacuated to a vacuum pressure of 4.3 x 10^{-6} Torr at ambient temperature. The beam was focused onto samples with a spot sized estimated to be 120 µm x 175 µm. The baseline and control data for the IBIL experiments are presented in Appendix A.

3.2 Results and Discussion

3.2.1 Synthesis and Characterization

In the presence of DMF as solvent, crystalline products were obtained for Compounds 1 (Sm-ADC), 2 (Eu-ADC), 3 (Tb-ADC), and 8 (Gd-ADC) and Nd-ADC. For Nd and Sm containing samples, small crystallites were obtained that were below the size that is suitable for SCXA. However, suitable sizes were obtained for Eu, Tb and Gd in DMF/H₂O. For Ce and Pr, no crystals were obtained in the DMF/H₂O solvent. With DEF as solvent, no crystal formation was observed for the metal/ligand ratios investigated (Figure 3.3).
Figure 3.3. Powder X-ray diffraction patterns of Nd-ADC, **Compounds 1-3, 8** and simulated diffraction pattern of **Compound 3** from SCXA.
SCXA crystal analysis was performed on the Eu-ADC, Tb-ADC, and Gd-ADC samples. Further attempts to synthesize larger crystals of Nd-ADC and Sm-ADC were made by changing the temperature to 80 and 125 °C and by extending the crystallization time to 1, 2, and 3 days were unsuccessful. The crystal sizes were observed with an optical microscope, and were less than 0.2 mm.

The PXRD patterns of the dried samples of Compounds 1, 2, 3, 8 and Nd-ADC along with the simulated profile of Compound 3 (from SCXA data presented later) are shown in Figure 3.3. The diffraction patterns show peaks in identical 2θ positions among the samples, indicating that the materials were isostructural. Except for Compound 8 (Gd-ADC), the MOFs have identical diffraction patterns to the simulated pattern represented by Compound 3, which suggests that the crystal structures remain intact upon vacuum drying. The PXRD patterns of the dried samples are identical to those simulated from SCXA data of the MOF crystals in the original synthesis mixtures, which means that the removal of uncoordinated solvent at room temperature does not affect crystal structure. The similarity in the PXRD patterns to their simulated patterns from SCXA data indicates that each sample crystallizes as a pure phase.

Based on its PXRD pattern, Compound 8, in its vacuum dried form, is isostructural with the others; however, SCXA data of the original sample shows that it is isostructural to MOFs reported in Chapter IV discussed later. Its structure is discussed in Chapter IV. We believe there was a structural transformation resulting from the removal of solvent guest molecules during the drying process.

Single crystal X-ray diffraction was conducted on Compounds 2 and 3. The single crystal structure parameters for Compounds 2 and 3 are presented in Table 3.1.
Powdered X-ray diffraction and elemental analysis were used to compare Compounds 1 (Sm-ADC), 2 (Eu-ADC), 3 (Tb-ADC), and Nd-ADC. Since all four materials are isostructural, analysis is discussed in detailed for Compound 3 as a representative of the others.

Table 3.1. Crystal structure refinement data for Compounds 2 and 3

<table>
<thead>
<tr>
<th></th>
<th>Compound 2</th>
<th>Compound 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{63}H_{59}N_{5}O_{17}Eu_{2}</td>
<td>C_{63}H_{59}N_{5}O_{17}Tb_{2}</td>
</tr>
<tr>
<td></td>
<td>[Eu_{2}(ADC)_{3}·5DMF]</td>
<td>[Tb_{2}(ADC)_{3}·5DMF]</td>
</tr>
<tr>
<td>Density g cm(^{-3})</td>
<td>1.645</td>
<td>1.681</td>
</tr>
<tr>
<td>(\mu/\text{mm}^{-1})</td>
<td>2.183</td>
<td>2.484</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1462.07</td>
<td>1475.99</td>
</tr>
<tr>
<td>Crystal System</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>(a/\text{\AA})</td>
<td>10.4144(5)</td>
<td>10.3706(9)</td>
</tr>
<tr>
<td>(b/\text{\AA})</td>
<td>11.4340(5)</td>
<td>11.3600(9)</td>
</tr>
<tr>
<td>(c/\text{\AA})</td>
<td>12.9875(6)</td>
<td>12.9850(11)</td>
</tr>
<tr>
<td>(\alpha/^\circ)</td>
<td>72.8203(11)</td>
<td>72.5410(10)</td>
</tr>
<tr>
<td>(\beta/^\circ)</td>
<td>89.9297(11)</td>
<td>89.7340(10)</td>
</tr>
<tr>
<td>(\gamma/^\circ)</td>
<td>87.1572(12)</td>
<td>87.4110(10)</td>
</tr>
<tr>
<td>(V/\text{\AA}^3)</td>
<td>1475.56(12)</td>
<td>1457.7(2)</td>
</tr>
</tbody>
</table>
For Compound 3, the crystal structure was refined to a P-1 space group and the triclinic crystal system. The unit cell dimensions are 10.4 Å x 11.4 Å x 12.9 Å. The volume of the unit cell is 1476 Å³ and the calculated density is 1.7 g/cm³.

The structure is comprised of three coordinating ADC ligands for every two trivalent lanthanide ions in a unit cell. Unit cell charge balance was achieved, since the number of ligands and their charge (2⁻ x 3 = 6⁻) is balanced to that of two trivalent lanthanides (3⁺ x 2 = 6⁺).

Figure 3.4 presents the coordination environment of Tb atoms and Table 3.2 presents selected bond lengths and bond angles for Compound 3. There are five ADC molecules and two DMF molecules surrounding each Tb₁ ion. With a total of nine Tb₁-O bonds, seven Tb₁-O bonds are with the oxygens from five ADC ligands and two Tb₁-O bonds are with oxygens of two DMF molecules. The ADC Tb₁-O bond lengths range from 2.322 to 2.543 Å, and the DMF Tb-O bond lengths range from 2.380 to 2.421 Å, similar to those observed in coordination polymers.³⁵,³⁸
Figure 3.4. Coordination environment of Tb1 in **Compound 3**. Hydrogen atoms omitted for clarity.

The coordination geometry for the Tb1 conforms to an irregular tricapped trigonal prismatic polyhedron with nine coordinating oxygen atoms and, there are two crystallographically identical Tb ions per unit cell (Figure 3.5). Two Tb ions are bridged by the oxygens of two ADC ligands with O1 atoms coordinating Tb1 ions creating a Tb1…Tb1 distance of 3.998 \(\text{Å}\).
Figure 3.5. Tricapped trigonal prismatic polyhedra linked through the oxygen of chelating ADC. (Ligands removed for clarity).

Table 3.2. Selected bond lengths and bond angles for **Compound 3**

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb1—O1</td>
<td>2.414</td>
</tr>
<tr>
<td>Tb1—O1</td>
<td>2.543</td>
</tr>
<tr>
<td>Tb1—O2</td>
<td>2.513</td>
</tr>
<tr>
<td>Tb1—O3</td>
<td>2.322</td>
</tr>
<tr>
<td>Tb1—O4</td>
<td>2.437</td>
</tr>
<tr>
<td>Tb1—O5</td>
<td>2.456</td>
</tr>
<tr>
<td>Tb1—O6</td>
<td>2.437</td>
</tr>
<tr>
<td>Tb1—O7</td>
<td>2.380</td>
</tr>
<tr>
<td>Tb1—O8</td>
<td>2.421</td>
</tr>
</tbody>
</table>

The Voronoi Dirichlet Polyhedral (VDP) of Tb1 can be considered as the geometrical image of the corresponding atom in the crystal field (Figure 3.6). Tb1
atomic attributes are $V_{\text{VDP}} = 11.54 \, \text{Å}^3$ and $S_{\text{VDP}} = 28.49 \, \text{Å}^2$, where $V_{\text{VDP}}$ is the atomic volume of the VDP and the $S_{\text{VDP}}$ is the atomic surface area of the VDP. The VDP parameters are within observed values for nine coordinate lanthanide ions in crystal lattices.$^{65}$

![Diagram of nine faced VDP of Tb1](image)

Figure 3.6. Nine faced VDP of Tb1 represented as polyhedra in **Compound 3**. (Ligands are removed for clarity).

The ADC ligand is present in three coordination modes which are presented in Figure 3.7. The coordination modes are $\mu_2:\eta_3$ (bridging-chelating), $\mu_2:\eta_2$ (bridging), and $\eta_2$ (bis-chelating). The bridging ligands involve linking four metals together, whereas the bis-chelating ligands only involve linking two metals.
Figure 3.7. The ADCH$_2$ coordination modes in **Compound 3** as a) bridging-chelating, b) bridging, and c) bis-chelating.

Along the [100] direction, the ligand is connected to the Tb1 ions in bis-chelating coordination mode (Figure 3.8a). Adjacent Tb1…Tb1 metal ions are connected by the carboxylates of a pair of ADC running almost perpendicular to the chain. A bridging ligand coordinates to four metal ions in the polymeric chain along the [010] direction (Figure 3.8b). In this case, the two adjacent metal atoms are bridged by intrachain ligand carboxylates. Along the [001] direction, a chain is present with the bridging chelating ligands connected through a pair of Tb1 ions (Figure 3.8c).
Figure 3.8. Metal-ligand chains in Compound 3 with the ligand in a) bis-chelating b) bridging and c) bridging-chelating coordination modes. (Hydrogen atoms are removed for clarity).

In the [100] direction, bridging metal-ADC chains creates a 2-D connection with the bis-chelating metal-ADC chain through intersecting bimetallic Tb…Tb centers (Figure 3.9).
Figure 3.9. Interconnectivity of two bridging chains in **Compound 3**. (Solvent and hydrogens omitted for clarity).

In the [010] direction, bridging-chelating and bis-chelating metal-ADC chains create a 2-D connection with bridging metal-ADC chain through intersecting bimetallic Tb…Tb centers (Figure 3.10).
Figure 3.10. Interconnectivity of bridging and bis-chelating chains in **Compound 3**. (Solvent and protons omitted for clarity).
Figure 3.11. 3-D crystal packing structure for **Compound 3** viewed along the [010] direction.
ADC units are present in the structure as a 3-D bimetallic cluster that makes up the multi-coordinate building block of the MOF. From this repeating unit, the cluster can span each direction, and is involved in the [100], [010], and [001] planes (Figure 3.12). The six ADC cluster contained two metal atoms and compares to that of the ZnO(COO)$_6$ secondary building unit (SBU) reported by Ma et al.$^{42}$ and Jung et al.$^{66}$

![Diagram of ADC ligands and metal ions](image)

Figure 3.12. Orientation of ADC ligands (grouped by color) at each bimetallic center. The red, blue and green colored tubes are ADC ligands and the purple tubes are metal ions.

Simplifying the structure using TOPOS$^{60}$ software reveals a network topology structure with Tb atoms and the ligands as nodes (Figure 3.13). To derive the net, the ADC ligands are reduced to 2-coordinate or 4-coordinate nodes depending on the
coordination mode of the ligand. For the bridging connection, the ligand is represented as a 4-coordinate node. For the bis-chelating connection, the ligand is represented as a 2-coordinate node. The Tb1 atoms are reduced to 4-coordinate nodes, omitting the presence of non-coordinated solvent molecules.

Figure 3.13. Simplified topology for **Compound 3** viewed along the [010] direction.

The FTIR spectra of **Compounds 1-3** and ADCH$_2$ powder are presented in (Figure 3.14). The band at 3448 cm$^{-1}$ indicates the presence of OH from adsorbed water species on the MOFs and on ADCH$_2$ powder. The 2925 cm$^{-1}$ and 2967 cm$^{-1}$ bands observed with the ADCH$_2$ are assigned to weakly intramolecular O···H bonds between non-planar C=O with H on the aromatic ring at the 1, 4 and 5, 8 carbon positions. These bands are not observed in **Compounds 1-3**, and their absence is attributed to the locked orientation of the ADC in the structures, limiting the interaction of C=O with aromatic H.
The band observed at 1687 cm$^{-1}$ in the ADCH$_2$ IR spectrum is attributed to the HO–C=O, with localized charges on the ligand’s carboxylic acid functional groups. This band is not observed for Compounds 1-3, indicating deprotonation of the ADCH$_2$ ligands to form ADC within the MOFs. Instead, the band observed at 1687 cm$^{-1}$ and is divided into individual bands at 1601 cm$^{-1}$ and 1551 cm$^{-1}$, which is attributed to C-O bonds and the variation in stretching vibrations for the three different ligand conformations. The band at 1562 cm$^{-1}$ bands can be found in the MOF spectra, indicative of metal-oxygen bonds.$^{67}$
Figure 3.14. FTIR Spectra of **Compounds 1-3** and ADCH₂.
The ADC-MOF samples were subjected to a post-synthesis chloroform exchange procedure to remove excess uncoordinated solvents from MOF structure. TGA was performed under a steady flow of nitrogen. Table 3.3 displays the % weight loss events for **Compounds 1-3**.

### Table 3.3. TGA weight loss events for **Compounds 1-3**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Event temp (°C)</th>
<th>Wt. loss(%)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 1</td>
<td>25–90</td>
<td>11</td>
<td>Adsorbed H₂O, CHCl₃</td>
</tr>
<tr>
<td></td>
<td>90-400</td>
<td>15</td>
<td>Coordinated DMF</td>
</tr>
<tr>
<td></td>
<td>400-500</td>
<td>40</td>
<td>ADC</td>
</tr>
<tr>
<td></td>
<td>560-900</td>
<td>31</td>
<td>Metal oxide residue (remaining)</td>
</tr>
<tr>
<td>Compound 2</td>
<td>25–90</td>
<td>8</td>
<td>Adsorbed H₂O, CHCl₃</td>
</tr>
<tr>
<td></td>
<td>90-460</td>
<td>12</td>
<td>Coordinated DMF</td>
</tr>
<tr>
<td></td>
<td>460-560</td>
<td>45</td>
<td>ADC</td>
</tr>
<tr>
<td></td>
<td>560-900</td>
<td>35</td>
<td>Metal oxide residue (remaining)</td>
</tr>
<tr>
<td>Compound 3</td>
<td>25–90</td>
<td>6</td>
<td>Adsorbed H₂O, CHCl₃</td>
</tr>
<tr>
<td></td>
<td>90-460</td>
<td>12</td>
<td>Coordinated DMF</td>
</tr>
<tr>
<td></td>
<td>460-560</td>
<td>51</td>
<td>ADC</td>
</tr>
<tr>
<td></td>
<td>560-900</td>
<td>27</td>
<td>Metal oxide residue (remaining)</td>
</tr>
</tbody>
</table>

In general, TGA of the samples depicted in Figure 3.15 shows small weight loss events at approximately 100 °C representing the loss of H₂O and CHCl₃ molecules.
(~10%). Steady loss of DMF is observed up until 200 °C; followed by ADC degradation approximately 460 °C. Residue of about 30% are attributed to the lanthanide oxides.
Figure 3.15. TGA curves for Compounds 1-3.
3.2.2 Photoluminescence

The photoluminescence spectra of Compounds 1-3 and ADCH$_2$ powder are presented in Figure 3.16. The excitation and emission spectra for ADCH$_2$ is similar to that reported for ADCH$_2$.\textsuperscript{68} Like ADCH$_2$ powder, Compounds 1-3 show excitation peaks in the 300-450 nm region and broad emission peaks in the 400-600 nm region. Therefore, emission peaks observed in Compounds 1-3 are ADC linker-based. Like ADCH$_2$, the spectra of Compounds 1-3 shows Stokes shift, the values of which are presented in Table 3.4. The Stokes shift is attributed to non-radiative relaxation pathways in the structures due to interactions between the neighboring chromophores of the MOF. Compound 1 displays the smallest Stokes shift (26 nm), the largest is with the ADCH$_2$ standard at 87 nm.

Figure 3.17 compares the emission spectral profiles of Compounds 1, 2, 3 ADCH$_2$, and ADC-Na in solution. The powdered solid ADCH$_2$ luminescence spectrum shows a broad featureless peak at $\lambda_{\text{max}}$ 500 nm. In the solid powdered form the individual ADCH$_2$ molecules are densely packed, which increases intermolecular interactions and shortens $\pi-\pi$ distances between aromatic faces of the anthracene moiety. This results in multiple non-radiative relaxation pathways for the excited molecules, which in turn red shifts the emission $\lambda$ and broadens the emission peak. Presumably, hydrogen bonding between terminal carboxylic acid groups introduces short interchromophore stacking distances as does the end-to-face herringbone packing arrangement of anthracene.\textsuperscript{68}
Normalized Intensity

Wavelength (nm)

Compound 1
Ex_435
Em_380

Normalized Intensity (a.u.)

Wavelength (nm)

Compound 2
Ex_435
Em_380

Normalized Counts

Wavelength (nm)

Compound 3
Ex_435
Em_380
Figure 3.16. Photoluminescence spectra for **Compounds 1-3** and the ADCH₂ powder.

The spectrum of an aqueous solution of ADC-Na shows a sharper peak profile and is significantly blue shifted relative to ADCH₂ powder. This is ascribed to the fact that the ADC units that are further apart have less distribution of the non-radiative relaxation pathways, hence increase the extent of higher energy electronic transitions.

Table 3.4 Stokes shift of **Compounds 1-3** and ADCH₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stokes Shift (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Compound 1) Sm-ADC</td>
<td>26</td>
</tr>
<tr>
<td>(Compound 2) Eu-ADC</td>
<td>80</td>
</tr>
<tr>
<td>(Compound 3) Tb-ADC</td>
<td>62</td>
</tr>
<tr>
<td>ADCH₂</td>
<td>87</td>
</tr>
</tbody>
</table>
The ADC-Na in dilute solution represents interchromophore coupling at its minimum and molecular spacing at its maximum show the highest energy for its $\pi^* \rightarrow \pi$ transition. Its spectrum matches that of anthracene in monomeric arrangement reported by Hinou et al.\textsuperscript{68}

Figure 3.17. Room temperature solid state photoluminescence emission spectra ($\lambda_{ex} = 380$ nm) for Compounds 1, 2, 3, ADCH\textsubscript{2} and ADC-Na as 1 mM solution in water.

**Compounds 1-3** exhibit $\lambda_{max}$ values between those of ADC-Na and ADCH\textsubscript{2}. The peaks observed and their associated vibronic transitions are presented in Table 3.5. Within a MOF, the spacing between ligands are fixed. Cofacial ADC units in the [100] direction are interrupted by ADC in the [010] direction. The distance is 14.5 Å between cofacial ADC which is beyond the distance for coupling interactions to occur (Figure 3.18).\textsuperscript{68}
Since the ligands are in an ordered, fixed orientation throughout the crystal, a more narrow distribution of vibronic level population is observed (Figure 3.18).

Figure 3.18. Arrangement of ADC units in **Compounds 1-3** exhibiting large intermolecular distances (14.5 Å) of neighboring moieties.

When the spacing is increased, the coupling between nearby chromophores lessens; therefore, higher energy emission is observed for **Compound 1**. The $\lambda_{\text{max}}$ is blue-shifted from the ADCH$_2$ (500 nm) at 433 nm. The blue-shifting is attributed to more spacing between chromophores in the MOF.

**Compound 3** exhibits a similar emission profile to **Compound 1**, with $\lambda_{\text{max}}$ blue-shifted to approximately 427 nm compared to ADCH$_2$. The peak profile is similar to that of ADC-Na in solution. This is also explained by limited interchromophore coupling due to rigid ligand spacing in the structure.$^{68}$ The reason for the enhanced peak around 470 nm in **Compound 2** containing europium ions is not clear, but could possibly be due to charge transfer from the ligand to europium, thereby reducing the metal from Eu$^{3+}$ to
Eu$^{2+}$. This lanthanide reduction by an organic ligand under radiation has been previously reported in a related Eu-ligand coordination compound.$^{69}$

Data observed for **Compounds 1-3** suggest that luminescence for the trivalent lanthanide ions are not observed due possibly to any of three reasons. Firstly, the ADC ligand is preferentially absorbing the UV radiation due to its high extinction coefficient versus low extinction coefficients for the lanthanide metal. Secondly, the radiation that does reach the lanthanides may undergo a back electron transfer mechanism that does not allow the lanthanide's characteristic emission peaks to be observed, due to the position of the inherent energy levels of ADC and the Sm$^{3+}$, Eu$^{3+}$, and Tb$^{3+}$ ions. Thirdly, there is little energy transfer between the triplet states of the ligand and the emissive energy states of the lanthanide atoms.

<table>
<thead>
<tr>
<th>Emission Transition</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1,0 → S0,0</td>
<td>406</td>
</tr>
<tr>
<td>S1,0 → S0,1</td>
<td>433</td>
</tr>
<tr>
<td>S1,0 → S0,2</td>
<td>463</td>
</tr>
<tr>
<td>S1,0 → S0,3</td>
<td>496</td>
</tr>
</tbody>
</table>

Time-resolved emission measurements were used to further investigate the local environment of the anthracene units of **Compounds 1-3** and were compared to that of ADCH$_2$. The intensity vs. time decay curves for **Compounds 1-3** and ADCH$_2$ are presented in Figure 3.19. The curves were fitted by a biexponential function as in
Equation 2. The lifetimes are presented in Table 3.6. The faster component ($\tau_1$) of the radiative lifetime of ADCH$_2$ powder was determined to be 7.1 ns. This is similar to the value reported for bulk anthracene in its end-to-face herringbone tightly packed structure.\textsuperscript{68} **Compounds 1, 2, and 3** exhibit lifetimes of $\tau_1 = 1.8, 1.9$, and 1.9 ns, respectively. The observed fast components are likely due to the emission from monomeric-like anthracene moieties, since the lifetimes closely resemble that of anthracene (2.0 ns) observed in a monomer arrangement.\textsuperscript{68}

The similarity in lifetimes of the MOFs is consistent with the similarity in the isostructural arrangement of ADC within their structures. A faster lifetime is observed for the MOFs compared with ADCH$_2$ ligand, and is consistent with the limited amount of non-radiative transitions that occur with the highly spaced ligands. The lifetime of the longer-lived component, $\tau_2$, is also attributed to the interchromophore distances. Emission from dimerized chromophores can increase the long lifetime components observed with ADCH$_2$ powder ($\tau_2 = 64.3$ ns).\textsuperscript{9} The $\tau_2$ for **Compounds 1, 2 and 3** are 19.1, 19.7, and 36.9 ns, respectively. The observed $\tau_2$ in **Compounds 1, 2, and 3** are shorter than that observed with ADCH$_2$ and this is attributed to the increased distance between ADC ligands in the structures.

Quantum efficiency (QE) is the ratio of photons emitted to the photons absorbed. It has been reported that the QE is greatly enhanced for an anthracene in its monomeric arrangement versus the end-to-face arrangement in bulk due to the absence of excimer formation upon irradiation.\textsuperscript{9,71} Excimer formation promotes the non-radiative decay process, so increased spacing between anthracene molecules increases the efficiency of light emission.\textsuperscript{68}
Figure 3.19. Fluorescent lifetime histograms of Compounds 1-3 and ADCH$_2$ with a model fit.
The reported QE for anthracene crystal in end-to-face herringbone arrangement is (QE = 0.02)\textsuperscript{68} and that of anthracene monomers in solution is (QE = 0.30).\textsuperscript{68,72} In this work, attempts to collect QE data on \textbf{Compounds 1, 2, and 3} produced inconsistent results amongst repeated analysis of each MOF. The discrepancies observed in the QE data in repeated MOF measurements may have arisen from the variations in crystal size and shape, as was visually observed. Similar observation of QE data with MOF crystal analysis was observed by Bauer et al.\textsuperscript{44} However, since \textbf{Compounds 1, 2 and 3} all resemble a monomeric arrangement of anthracene units, it is expected that more efficient luminescent pathways are available and their QE would increase over the bulk ADCH\textsubscript{2} value.

Table 3.6. Photoluminescence lifetimes of \textbf{Compounds 1-3} and ADCH\textsubscript{2} ligand

<table>
<thead>
<tr>
<th>Sample</th>
<th>Name</th>
<th>$\tau_1$ (ns)</th>
<th>% comp</th>
<th>$\tau_2$ (ns)</th>
<th>% comp</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADCH\textsubscript{2}</td>
<td>9,10-anthracenedicarboxylic acid</td>
<td>7.09</td>
<td>74</td>
<td>64.3</td>
<td>26</td>
</tr>
<tr>
<td>Compound 1</td>
<td>Sm-ADC MOF</td>
<td>1.78</td>
<td>69</td>
<td>19.1</td>
<td>31</td>
</tr>
<tr>
<td>Compound 2</td>
<td>Eu-ADC MOF</td>
<td>1.86</td>
<td>71</td>
<td>19.7</td>
<td>29</td>
</tr>
<tr>
<td>Compound 3</td>
<td>Tb-ADC MOF</td>
<td>1.86</td>
<td>71</td>
<td>36.9</td>
<td>29</td>
</tr>
</tbody>
</table>

\textbf{3.2.3 Radioluminescence}

IBIL was used to probe the radioluminescence characteristics of \textbf{Compounds 1-3} under 1.5 and 2.5 MeV ionizing proton beam. IBIL spectra were collected on a CCD spectrophotometer, and the emission decay was observed after the crystal was exposed to
the proton beam. The IBIL emission profiles are compared with photoluminescence spectra of Compounds 2, 3 and ADCH₂ in Figure 3.20. Compound 2 was used for the majority of the investigations because of its large crystal size with face sizes around 180 μm. The large size allowed the focus beam to readily interface with the crystal surface and not too easily penetrate through the crystal during data collection. A pronounced emission profile is observed in the IBIL spectra of Compounds 2, 3 and ADCH₂ with distinct maxima visible at 440, 440 and 515 nm, respectively. Similarity of the spectral profiles of Compounds 2 and 3 compared to ADCH₂ shows that the IBIL is a product of the MOF crystal only, and not of any ADCH₂ impurities from synthesis or a result of damage caused by the beam. The presence of the IBIL spectra validates the fact that ADCH₂ is radioluminescent (scintillating) and that ADC in the MOF structures remains scintillators. Compound 2 showed almost no red shift of the IBIL fluorescence peak compared to the photoluminescence peak. This indicates that the local environment of the ligand was not changed after the proton beam exposure. Similar results were observed for Compound 3. From the perspective of practical scintillator use, the IBIL spectra of Compounds 2 and 3 are comparable to their observed photoluminescence phenomena, exhibiting Stokes shifts of 54 and 69 nm, respectively. Therefore, minimal overlap exists between the optical absorption and IBIL emission which should favor radiation detection, since self- absorption should be minimal.⁹

A small red shift of the peak for Compound 3 similar to that of ADCH₂ after proton beam exposure may occur because of the increase in temperature at the focused proton beam, which may change the ADCH₂ ligands position slightly by structural damage.
Radioluminescence lifetime measurements were carried out for **Compounds 1, 2** and bulk anthracene. The samples were exposed to $^{137}$Cs ionizing radiation ($\gamma$ radiation) under experimental conditions given in Section 3.4.
Figure 3.20. IBIL emission spectral profiles compared with the photoluminescence spectra of Compounds a) 2, b) 3, and c) ADCH$_2$

Anthracene crystal was used as a reference because the ADCH$_2$ showed no coincident peaks upon PMT trigger during TCSPC measurements therefore its histogram could not be established. The gamma radiating cesium source did not produce light emission from an ionized ADCH$_2$ standard. It is unclear as to why this phenomenon was observed. However, it is reported$^{73}$ that the carboxylate functional groups can change their nuclear geometry in the excited state to a near coplanar conformation of anthracene backbones which increases resonance and $\pi$-$\pi$ overlap between ligand molecules (Figure 3.21), eliminating fluorescence. The intensity vs. time decay curves are presented in (Figure 3.22). The data was fitted to a biexponential function with Equation 2 and lifetime data are presented in Table 3.7.

The radiation lifetime measurements show that the major components’ scintillation lifetime is around 6 ns compared to its fluorescence lifetime around 2 ns.
The scintillation lifetime for the MOFs are shorter than the lifetime observed for the anthracene crystal.

![Diagram of conformation change](image)

Figure 3.21. Conformation change of ADCH$_2$ due to free rotation of carboxylate functional group during excitation processes.$^{73}$

For anthracene, the major component $\tau_1$ has a lifetime of 7 ns. The $\tau_1$ value for Compounds 1 and 3 is 6 ns which is comparable to anthracene. More data points were collected for anthracene vs. Compounds 1-3, hence the data presented for Compounds 1-3 are considered preliminary. Because of its higher bulk density compared to Compounds 1-3, anthracene yielded many more data points in a short time compared to Compounds 1-3.
Figure 3.22. Radioluminescence intensity vs. time decay curves for Compounds 1-3 and anthracene at room temperature from TCSPC.
Further investigation into the scintillation lifetime would be necessary to understand the variations in short and long components of this MOF series. Compound 2’s fast component is unusual, so further investigation will be necessary to provide clarification.

Table 3.7. Scintillation lifetime measurements for Compounds 1-3 and anthracene

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_1$ (ns)</th>
<th>Comp (%)</th>
<th>$\tau_2$ (ns)</th>
<th>Comp (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 1</td>
<td>6.0</td>
<td>29</td>
<td>10</td>
<td>71</td>
</tr>
<tr>
<td>Compound 2</td>
<td>2.0</td>
<td>36</td>
<td>10</td>
<td>64</td>
</tr>
<tr>
<td>Compound 3</td>
<td>6.0</td>
<td>25</td>
<td>10</td>
<td>75</td>
</tr>
<tr>
<td>Anthracene</td>
<td>7.0</td>
<td>83</td>
<td>19</td>
<td>17</td>
</tr>
</tbody>
</table>

Studies were performed to investigate how emission decay was affected by the beam current density and radiation dose on Compound 2. The emission peak spectral profiles are plotted vs. proton beam exposure time (PBET) at different current densities (Figure 3.23). For each beam current density, the normalized intensity was plotted versus the proton beam dose and compared.

The IBIL fluorescence was recorded for Compound 3 and ADCH$_2$ at a beam current of 2.5 MeV and current density of 12000 nA/cm$^2$ (Figure 3.24). In all cases, the emission intensities decreased with exposure time, signifying radiation damage by the proton beam. As the current density increased, the spectral profile of Compound 2 became more pronounced.
Figure 3.23. IBIL fluorescence (intensity vs. exposure time and dose) for **Compound 2** at different beam current densities: a) 472, b) 1330, c) 2700 nA/cm² and d) dose.
The intensities of the IBIL emission spectrum maximum for **Compound 3** and ADCH$_2$ were used to compare the rate of intensity degradation with radiation dose. The solid lines are fits of the maximum IBIL intensity for ADCH$_2$ (515 nm) and **Compound 3** (440 nm) to a stretched exponential function, as shown in Equation 3 (Figure 3.24).

The decay constants, $D_0$, for **Compound 3** and ADCH$_2$ are presented in Table 3.8. The decay constant is high for **Compounds 2** and 3, which translates to a high resistance to radiation damage from the 2.5 MeV proton beam.

The high current densities needed to observe degradation also reflect the resistivity of the MOFs to radiation damage (Figure 3.25). Related reported experiments utilized lower current densities of 100 and 500 nA/cm$^2$. Current densities up to 472 nA/cm$^2$ caused little damage to the MOFs with applied proton beam exposure times.
Figure 3.24. a) IBIL decay profile of Compound 3 and ADCH$_2$ after ion beam exposure with a beam energy of 2.5 MeV and 12000 nA/cm$^2$ current. b) Normalized intensities of dose-dependent IBIL spectra for Compound 3 compared to ADCH$_2$ crystal, with 12000 nA/cm$^2$ beam current at 2.5 MeV beam energy. (No data was detected beyond a dose of 4 x 10$^{15}$/cm$^3$ for ADCH$_2$).
Table 3.8. Comparison of decay constants for Compounds 2, 3 and ADCH$_2$ ligand reference solid

<table>
<thead>
<tr>
<th>Sample</th>
<th>Current Dens. (nA/cm$^2$)</th>
<th>Beam Energy (MeV)</th>
<th>D$_0$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 3</td>
<td>12000</td>
<td>2.5</td>
<td>$7.25 \times 10^{-3}$</td>
<td>0.338</td>
</tr>
<tr>
<td>ADCH$_2$</td>
<td>12000</td>
<td>2.5</td>
<td>$1.51 \times 10^{-3}$</td>
<td>0.326</td>
</tr>
</tbody>
</table>

Figure 3.25. Optical micrographs of a) ADCH$_2$ and b) Compound 2 at a beam energy of 2.5 MeV, before (left) and after (right) a dose of $3 \times 10^{15}$ /cm$^2$. 
CHAPTER IV

SYNTHESIS AND PHOTO- RADIOLUMINESCENCE INVESTIGATIONS OF MOFS FROM ANTHRACENE AND LATE PERIOD LANTHANIDE IONS

4.0 Introduction

Following the successful synthesis of Ln-ADC MOFs with earlier period lanthanide ions, the late period lanthanide metals (dysprosium through ytterbium) with smaller atomic radii were explored to coordinate with the ADCH\textsubscript{2} ligand. These ions have progressively smaller radii and their impact on the synthesis of Ln-ADC structures and the resulting luminescence properties were of interest. The metal:ligand ratio used in these experiments was 2:1. Five novel Ln-ADC structures Compounds 4 (Ho-ADC), 5 (Er-ADC), 6 (Tm-ADC), 7 (Ho-ADC) were synthesized. Compound 8 (Gd-ADC) was found to be isostructural with this set of MOFs using SCXA data.

4.1 Experimental Method

As in Chapter III, DMF and water were used as solvents at 100 °C. The progress of crystallization was monitored daily by visual observation of the MOF synthesis vial. Characterization methods previously reported in Chapter III were employed.

**Compound 4** (\(C_{60}H_{58}N_4O_{19}Ho_2\)): A mixture of Ho(NO\textsubscript{3})\textsubscript{3}•6 H\textsubscript{2}O (0.1 mmol, 0.044 g), ADCH\textsubscript{2} (0.05 mmol, 0.013 g) and DMF/H\textsubscript{2}O (10 mL/ 10 mL) were sealed in a 20 mL scintillation vial and heated to 105°C for 72 h in a convection oven. The vial was
The vial was allowed to cool to room temperature and the colorless crystals were filtered under vacuum and repeatedly washed with fresh DMF at room temperature. (Yield = 71%, 0.012 g, based on ADC\(\text{H}_2\)). Elemental Anal. (%): C, 48.79; H, 3.77; N, 3.71. Calcd. (%): C, 49.04; H, 3.95; N, 3.81. IR (KBr pellet, cm\(^{-1}\)): 3341br, 1562s, 1450m, 1327s, 1284m, 1176w, 1105br, 1029w, 839s, 794m, 736m, 686s, 600w, 468m.

**Compound 5** (C\(_{60}\)H\(_{58}\)N\(_4\)O\(_{19}\)Er\(_2\)): The synthesis procedure was similar to **Compound 4** except Er(NO\(_3\))\(_3\)•6 H\(_2\)O was used as the lanthanide metal salt (0.1 mmol, 0.044 g). The vial was allowed to cool to room temperature and the colorless crystals were filtered under vacuum and repeatedly washed with fresh DMF at room temperature. (Yield = 71%, 0.012 g, based on ADCH\(_2\)). Elemental Anal. (%): C, 49.00; H, 3.98; N, 3.75. Calcd. (%): C, 50.70; H, 3.95; N, 4.69. IR (KBr pellet, cm\(^{-1}\)): 3341br, 1562s, 1450m, 1327s, 1284m, 1176w, 1105w, 1029w, 839s, 794m, 736m, 686s, 600w, 468m.

**Compound 6** (C\(_{60}\)H\(_{58}\)N\(_4\)O\(_{19}\)Tm\(_2\)): The synthesis procedure was similar to **Compound 4** except Tm(NO\(_3\))\(_3\)•6 H\(_2\)O was used as the lanthanide metal salt (0.1 mmol, 0.045 g). The vial was allowed to cool to room temperature and the colorless crystals were filtered under vacuum and repeatedly washed with fresh DMF at room temperature. (Yield = 65%, 0.011 g, based on ADCH\(_2\)). Elemental Anal. (%): C, 41.74; H, 3.56; N, 3.19. Calcd. (%): C, 48.70; H, 3.93; N, 3.79. IR (KBr pellet, cm\(^{-1}\)): 3341br, 1562s, 1450m, 1327s, 1284m, 1176w, 1105w, 1029w, 839s, 794m, 736m, 686s, 600w, 468m.

**Compound 7** (C\(_{60}\)H\(_{58}\)N\(_4\)O\(_{19}\)Yb\(_2\)): The synthesis procedure was similar to **Compound 4** except Yb(NO\(_3\))\(_3\)•6 H\(_2\)O was used as the lanthanide metal salt (0.1 mmol, 0.045 g). The vial was allowed to cool to room temperature and the colorless crystals were filtered under vacuum and repeatedly washed with fresh DMF at room temperature.
(Yield = 65%, 0.011 g, based on ADC). Elemental Anal. (% C, 45.75; H, 3.71; N, 3.39. Calcd. (% C, 48.51; H, 3.90; N, 3.77. IR (KBr pellet, cm⁻¹): 3341br, 1562s, 1450m, 1327s, 1284m, 1176w, 1105w, 1029w, 839s, 794m, 736m, 686s, 600w, 468m.

**Compound 8** (C₆₀H₅₈N₄O₁₉Gd₂): The synthesis procedure was similar to **Compound 4** except Gd(NO₃)₃•6H₂O was used as the lanthanide metal salt (0.1 mmol, 0.045 g). The vial was allowed to cool to room temperature and the colorless crystals were filtered under vacuum and repeatedly washed with fresh DMF at room temperature. (Yield = 94%, 0.012 g, based on ADC). Elemental Anal. (% C, 45.75; H, 3.71; N, 3.39. Calcd. (% C, 48.51; H, 3.90; N, 3.77.

**Compound 9** (C₆₀H₅₈N₄O₁₉Dy₂): The synthesis procedure was similar to **Compound 4** except Dy(NO₃)₃•6H₂O was used as the lanthanide metal salt (0.1 mmol, 0.035 g). The vial was allowed to cool to room temperature and the colorless crystals were filtered under vacuum and repeatedly washed with fresh DMF at room temperature. (Yield = 71%, 0.012 g, based on ADC). Elemental Anal. (% C, 49.04; H, 3.76; N, 3.22. Calcd. (% C, 50.98; H, 3.98; N, 4.72.

### 4.2 Results and Discussion

The crystals for the Ho-ADC and Yb-ADC were small and not suitable for SCXA. The structures of Dy-ADC, Er-ADC, Tm-ADC, and Gd-ADC MOFs were identified using SCXA. Figure 4.1 presents the X-ray diffraction patterns for **Compounds 4-7, 9**, and the simulated pattern for 6. The patterns suggested an entirely new MOF structure. The crystal structure of Gd-ADC (**Compound 8**) from the previous set of MOFs (Chapter III) is similar to those of **Compounds 4-7, and 9**. However, the
PXRD pattern of Dy-ADC did not match the PXRD patterns of the newly synthesized MOFs, represented by Ho-ADC. Both Gd-ADC and Dy-ADC structures undergo structural changes after vacuum filtration, which does not make them suitable for scintillation applications and thus, they were not investigated further.
Figure 4.1. Powdered X-ray diffraction pattern of Compounds 4-7, 9, and the simulated pattern of Compound 6.
4.2.1 Synthesis and Characterization

The PXRD patterns of Compounds 4-7, and 9 along with the simulated profile for Compound 6 are shown in Figure 4.1. The diffraction patterns show peaks in identical 2θ positions, indicating that the crystal structures are isomorphous. The MOFs show identical diffraction patterns to the simulated patterns from SCXA data represented by Compound 6, which suggest that the crystal structure remains intact upon vacuum drying. The PXRD patterns of the dried samples are identical to those of the MOF crystals in the original synthesis mixtures, which signifies removal of uncoordinated solvent at room temperature does not affect crystal structure. The similarity in the PXRD patterns to that of the SCXA simulated pattern indicates that each sample crystallizes as a pure phase.

Single crystal X-ray diffraction was conducted on Compounds 5, 6, 8 and 9. Powdered X-ray diffraction and elemental analyses were used to compare Compounds 5 (Er-ADC), 6 (Tm-ADC), and 8 (Gd-ADC). It was found that all three materials are isostructural; therefore, structural analysis is detailed only for Compound 6.

For Compound 6, the crystal structure was refined to a P-1 space group and the triclinic crystal system. The unit cell dimension for each crystal is approximately 12.6 Å x 14.9 Å x 17.1 Å. The volume of the unit cells is approximately 2879 Å³. The calculated densities of the crystals are approximately 1.7 g/cm³.

The MOF is comprised of three coordinating ADC ligands for every two trivalent lanthanide ions in a unit cell. Unit cell charge balance was achieved, since the number of ligands and their charge (2⁻ x 3 = 6⁻) is equal to two trivalent lanthanides (3⁺ x 2 = 6⁺).
Four DMF solvent molecules (one coordinated solvent), three water molecules (one coordinated water) are within the lanthanide sphere, and have zero charge.
Table 4.1. Crystal structure refinement for **Compounds 5-6, 8-9**

<table>
<thead>
<tr>
<th></th>
<th>5</th>
<th>6</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
</table>
| Formula | C_{60}H_{58}N_{4}O_{19}Er_{2}  
[Er_{2}(ADC)_{3}·4DMF·3H_{2}O] | C_{60}H_{58}N_{4}O_{19}Tm_{2}  
[Tm_{2}(ADC)_{3}·4DMF·3H_{2}O] | C_{60}H_{58}N_{4}O_{19}Gd_{2}  
[Gd_{2}(ADC)_{3}·4DMF·3H_{2}O] | C_{60}H_{58}N_{4}O_{19}Dy_{2}  
[Dy_{2}(ADC)_{3}·4DMF·3H_{2}O] |
| Density g cm\(^{-3}\) | 1.697 | 1.703 | 1.679 | 1.673 |
| Formula Weight | 1473.62 | 1476.96 | 1453.60 | 1464.10 |
| Crystal System | triclinic | triclinic | triclinic | triclinic |
| Space Group | P-1 | P-1 | P-1 | P-1 |
| a/Å | 12.6026(14) | 12.5949(3) | 12.596(3) | 12.6415(8) |
| b/Å | 14.9605(16) | 14.9329(4) | 14.936(3) | 15.0160(9) |
| c/Å | 17.1024(19) | 17.1174(5) | 17.080(4) | 17.1252(10) |
| α/° | 87.5905(14) | 87.538(2) | 87.526(3) | 87.549(2) |
| β/° | 69.7644(15) | 69.7810(10) | 69.815(3) | 69.694(2) |
| γ/° | 72.8494(14) | 72.8160(10) | 72.801(3) | 72.802(2) |
| V/Å\(^{3}\) | 2884.5(5) | 2879.8(8) | 2875.1(11) | 2905.9(3) |
Figure 4.3 presents the coordination environment of Tm atoms and Table 4.2 presents selected bond lengths and bond angles. The structure is a complex 3-D MOF consisting of two crystallographically inequivalent Tm atoms, six ADC ligands, two coordinated DMF, two lattice DMF, two coordinated water, and one lattice water molecule.

The coordination number of the thulium, Tm1, is eight. Six Tm1-O bonds are with oxygen atoms from four ADC ligands. The Tm1O₈ polyhedron is an irregular trigonal dodecahedral prism. One Tm1-O bond is with one water molecule and one Tm1-O bond is with a DMF molecule. The Tm1-O bond lengths range from 2.228(2) to 2.512(3) Å with an average bond length of 2.34(5) Å, while the O-Tm1-O angles range from 53.7(8)° to 89.1(4)°.

The second symmetry independent metal, Tm2, coordinates with seven oxygen atoms with the Tm2O₇ polyhedron in an irregular pentagonal bipyramid. Five Tm2-O oxygen atoms are from four ADC ligands and two Tm2-O bonds are with oxygens of DMF and water. The Tm2-O bond lengths range between 2.219(3) and 2.393(3) Å, with an average bond length of 2.286 Å. O-Tm2-O bond angles range from 55.69(3) to 86.29(2)°. Select bond angles are shown in Table 4.2. The DMF Tm-O bond lengths are approximately 2.30 Å and the water Tm-O bonds are around 2.30 Å as well. The Tm1…Tm2 distance is 4.687 Å. A list of select bond lengths and angles are presented in Table 4.2.

Tm1 and Tm2 atomic attributes are nearly identical, at V_{VDP}= 10.75 Å³, S_{VDP}= 27.72 Å². The VDP parameters are well within observed values for 7 and 8 coordinate lanthanide ions in crystal lattices.⁶⁵
Figure 4.2. Eight and seven faced VDP. (Ligands omitted for clarity).
Figure 4.3. Coordination environments of a) Tm1 and b) Tm2 in Compound 6. (Hydrogen atoms omitted for clarity).
Table 4.2. Selected bond lengths and angles for **Compound 6**

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tm1-O1 2.346</td>
<td>O10-Tm1-O1W 78.883</td>
</tr>
<tr>
<td>Tm1-O1W 2.295</td>
<td>O10-Tm1-O3 88.779</td>
</tr>
<tr>
<td>Tm1-O2 2.518</td>
<td>O10-Tm1-O4 89.250</td>
</tr>
<tr>
<td>Tm1-O3 2.447</td>
<td>O10-Tm1-O2 75.710</td>
</tr>
<tr>
<td>Tm1-O4 2.304</td>
<td>O10-Tm1-O1W 78.482</td>
</tr>
<tr>
<td>Tm1-O7 2.301</td>
<td>O10-Tm1-O14 86.015</td>
</tr>
<tr>
<td>Tm1-O10 2.225</td>
<td>O10-Tm1-O1 79.056</td>
</tr>
<tr>
<td>Tm1-O14 2.302</td>
<td>O7-Tm1-O1W 78.482</td>
</tr>
<tr>
<td>Tm2-O2W 2.328</td>
<td>O7-Tm1-O14 86.015</td>
</tr>
<tr>
<td>Tm2-O5 2.391</td>
<td>O7-Tm1-O1 79.056</td>
</tr>
<tr>
<td>Tm2-O6 2.318</td>
<td>O7-Tm1-O2 78.369</td>
</tr>
<tr>
<td>Tm2-O8 2.234</td>
<td>O1W-Tm1-O14 75.406</td>
</tr>
<tr>
<td>Tm2-O9 2.268</td>
<td>O1W-Tm1-O3 78.007</td>
</tr>
<tr>
<td>Tm2-O11 2.291</td>
<td>O14-Tm1-O3 78.814</td>
</tr>
<tr>
<td>Tm2-O13 2.212</td>
<td>O14-Tm1-O1 77.338</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
ADC is present in three coordination modes, namely, bridging ($\mu_2:\eta_2$), bis-chelating ($\eta_2$), and bis-monodentate ($\eta_1$), which are presented in Figure 4.4. The coordinated ligands are nearly perpendicular (102.41°), (111.86°), and (128.34) between the plane of the anthracene backbone and the carboxylate.

The bis-monodentate ($\eta_1$) coordination mode of the ADC has not been previously reported in ADC-MOFs. The uncoordinated oxygen forms a hydrogen bond with a nearby water molecule, thereby stabilizing the ligand by preventing it from free rotation (Figure 4.5).

Along the [010] direction the bridging ligands are observed (Figure 4.6). A 2-D “Ladder” conformation for the bis-chelating metal-ADC chains is observed, with the ladder rungs comprised of the bis-chelating ADC ligand and two coordinating Tm1 and Tm2 ions (Figure 4.4b). The “ladder” structure is similar to that reported by Wang et al. Along the ADC in the [010] plane, the rungs separate Tm1 and Tm2 by 11.212 Å.
Figure 4.4. Coordination modes of ADC in Compound 6 as a) bridging, b) bis-chelating and c) bis-monodentate.
Figure 4.5. Hydrogen bonding between ADC and water molecule coordinated to Tm2 in Compound 6.

Figure 4.6. a) 2-D polymeric chain with bridging ligands and b) polymeric chain in “ladder” conformation, comprised of two unique ligands and metals in Compound 6.
In the [100] direction, bridging ADC creates a 2-D connection with the bis-chelating ADC ligands. The bridging ligands intersect the bis-chelating ligands at bimetallic centers. In the [010] direction, bis-chelating ligands and bis-monodentate ADC ligands alternate connectivity between sets of bimetallic clusters. The bridging ADC ligands connect bimetallic clusters perpendicular to the bis-chelating and bis-monodentate ligands.

Figure 4.9 presents 3-D crystal packing of **Compound 6** viewed along the [010] axis. Small inaccessible pores are observed in this direction.

The ADC units are present as a 3-D bimetallic cluster that makes up the multicoordinate building block of the structure. From this repeating unit, the cluster spans each direction, and is involved in the [100], [010], and [001] planes (Figure 4.10). The networks stem from the nonequivalent Tm metals and the surrounding six ligands that are multidirectional facilitating connectivity.
Figure 4.7. Interconnectivity of two bridging chains in Compound 6. (Solvent and hydrogens omitted for clarity).
Figure 4.8. Interconnectivity of two bridging chains in **Compound 6**. (Solvent and hydrogens omitted for clarity).
Figure 4.9. The 3-D crystal structure packing along the [010] axis of Compound 6. (Uncoordinated solvent was omitted for clarity).
Figure 4.10. Multidimensional coordination center incorporating two Tm ions and six ADC ligands in Compound 6. The ADC ligands are colored green, blue, and red.

Simplifying the structure using TOPOS66 reveals a network topology with Tm atoms and the ADC ligands as nodes. To derive the net structure, bis-chelating and bis-monodentate ADC ligands are reduced to blue 2-coordinate nodes, and the bridging ligands are reduced to 4-coordinate blue nodes. The Tm1 atoms are reduced to pink 4-coordinate nodes, omitting the presence of coordinated solvent molecules (DMF and H2O)(Figure 4.11).
Figure 4.11. Topology of Compound 6 viewed along the [100] direction.

The FTIR spectra of Compounds 4-7 and ADCH$_2$ powder are presented in Figure 4.12. The band at 3448 cm$^{-1}$ indicates presence of OH as adsorbed water species on the MOF and on ADCH$_2$ powder. The 2925 cm$^{-1}$ and 2967 cm$^{-1}$ bands observed with the ADCH$_2$ ligand indicates weakly intramolecular bonded O···H bonds between non-planar C=O interactions with H on the aromatic ring at the 1,4 and 5,8 carbon positions. These bands are not observed in Compounds 1-3 and their absence is attributed to the locked orientation of the ADC in the structures, limiting interaction of C=O with aromatic Hs. The band observed at 1687 cm$^{-1}$ in the ADCH$_2$ IR spectra is attributed to the HO–C=O, with localized charges on the ligand’s carboxylic acid functional groups. This band is not observed in Compounds 4-7, indicating deprotonation of the ADCH$_2$ ligands to form ADC within the MOFs. Instead, the band observed at 1687 cm$^{-1}$ and is divided into individual bands at 1686 cm$^{-1}$, 1601 cm$^{-1}$, and 1551 cm$^{-1}$, which is attributed to C-O
bonds and the variation in stretching vibrations for the three different ligand conformations. The 1562 cm$^{-1}$ bands can be found in the MOF spectra, and is attributed to the metal-oxygen bonds.$^{67}$
Figure 4.12. FTIR spectra of **Compounds 4-7** and ADCH$_2$. 
Table 4.3 shows weight loss events for **Compounds 4-7**. In general, TGAs of the samples depicted in Figure 4.13 show small % weight loss event at approximately 100 °C accounting for loss of H₂O molecules (~10 %). Steady decline is observed for loss of DMF molecules up till 200 °C followed by ADC degradation onset at approximately 460 °C. Residues of amount to about ~ 20 % are attributed to the lanthanide oxides.
Table 4.3. **Compounds 4-7** weight loss events

<table>
<thead>
<tr>
<th>Compound 4</th>
<th>Event Temp (°C)</th>
<th>Wt. loss (%)</th>
<th>Molecular assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 - 90</td>
<td>11</td>
<td>Adsorbed H$_2$O, CHCl$_3$ from solvent exchange procedure</td>
</tr>
<tr>
<td></td>
<td>90- 400</td>
<td>15</td>
<td>Coordinated DMF</td>
</tr>
<tr>
<td></td>
<td>400-500</td>
<td>40</td>
<td>ADC</td>
</tr>
<tr>
<td></td>
<td>560-900</td>
<td>31</td>
<td>Metal oxide residue (remaining)</td>
</tr>
<tr>
<td>Compound 5</td>
<td>25 - 90</td>
<td>8</td>
<td>Adsorbed H$_2$O, CHCl$_3$</td>
</tr>
<tr>
<td></td>
<td>90- 460</td>
<td>12</td>
<td>Coordinated DMF</td>
</tr>
<tr>
<td></td>
<td>460-560</td>
<td>45</td>
<td>ADC</td>
</tr>
<tr>
<td></td>
<td>560-900</td>
<td>35</td>
<td>Metal oxide residue (remaining)</td>
</tr>
<tr>
<td>Compound 6</td>
<td>25 - 90</td>
<td>6</td>
<td>Adsorbed H$_2$O, CHCl$_3$</td>
</tr>
<tr>
<td></td>
<td>90- 460</td>
<td>12</td>
<td>Coordinated DMF</td>
</tr>
<tr>
<td></td>
<td>460-560</td>
<td>51</td>
<td>ADC</td>
</tr>
<tr>
<td></td>
<td>560-900</td>
<td>27</td>
<td>Metal oxide residue (remaining)</td>
</tr>
<tr>
<td>Compound 7</td>
<td>25 - 90</td>
<td>6</td>
<td>Adsorbed H$_2$O, CHCl$_3$</td>
</tr>
<tr>
<td></td>
<td>90- 460</td>
<td>12</td>
<td>Coordinated DMF</td>
</tr>
<tr>
<td></td>
<td>460-560</td>
<td>51</td>
<td>ADC</td>
</tr>
<tr>
<td></td>
<td>560-900</td>
<td>27</td>
<td>Metal oxide residue (remaining)</td>
</tr>
</tbody>
</table>
Figure 4.13. TGA curves of Compounds 4-7.
4.2.2 Photoluminescence

The photoluminescence spectra of **Compounds 4-7** and ADCH\(_2\) are presented in Figure 4.14. Like ADCH\(_2\) powder, **Compounds 4-7** show excitation peaks in the 300-450 nm region and broad emission peaks in the 400-600 nm region. The emission peaks observed in **Compounds 4-7** are therefore ADC linker-based. Like ADCH\(_2\), the spectra of **Compounds 4-7** shows Stokes shift (Table 4.4). **Compound 6** exhibits the smallest Stokes shift (27 nm), whereas the largest is ADCH\(_2\) at 87 nm.

Table 4.4. Stokes shifts of **Compounds 4-7** and ADCH\(_2\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stokes Shift Ex (nm)-Em (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Compound 4) Ho-ADC</td>
<td>59</td>
</tr>
<tr>
<td>(Compound 5) Er-ADC</td>
<td>40</td>
</tr>
<tr>
<td>(Compound 6) Tm-ADC</td>
<td>27</td>
</tr>
<tr>
<td>(Compound 7) Yb-ADC</td>
<td>29</td>
</tr>
<tr>
<td>ADCH(_2)</td>
<td>87</td>
</tr>
</tbody>
</table>

Figure 4.15 compares the emission spectral profiles of **Compounds 4-7**, ADCH\(_2\), and ADC-Na in water. The powdered solid ADCH\(_2\) luminescence spectrum is presented as a broad, featureless peak approximately 500 nm. The ADC-Na spectrum has a sharper peak profile, and is significantly blue shifted relative to ADCH\(_2\).
Table 4.5. Vibronic level assignments from luminescence spectra

<table>
<thead>
<tr>
<th>Emission Transition</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{1,0} \rightarrow S_{0,0}$</td>
<td>406</td>
</tr>
<tr>
<td>$S_{1,0} \rightarrow S_{0,1}$</td>
<td>433</td>
</tr>
<tr>
<td>$S_{1,0} \rightarrow S_{0,2}$</td>
<td>463</td>
</tr>
<tr>
<td>$S_{1,0} \rightarrow S_{0,3}$</td>
<td>496</td>
</tr>
</tbody>
</table>

Compounds 4-7 exhibit $\lambda_{\text{max}}$ between ADC-Na and ADCH₂. The ADC-Na and ADCH₂ samples were previously described in Chapter III. Compound 5 exhibits a similar emission profile as Compound 7, with blue-shifting observed at 427 nm compared to ADCH₂ (500 nm). The peak profile of Compound 6 $\lambda_{\text{max}}$ is blue-shifted from the ADCH₂ and its spectral peak profile is similar to that of ADC-Na. This is evidence of the interchromophore coupling limitations in the MOF compared to ADCH₂. The $\lambda_{\text{max}}$ for Compound 4 is blue-shifted from that of ADCH₂, but exhibits a completely different emission peak profile from the other MOFs. The change in peak profile is not clear, but may be due to the presence of the lanthanide ion, Ho$^{3+}$. 
Figure 4.14. Photoluminescence spectra for **Compounds 4-7** and the ADCH$_2$ powder.
Figure 4.15. Room temperature solid state photoluminescence emission spectra ($\lambda_{\text{ex}} = 380$ nm) for Compounds 4-7, ADCH$_2$ and ADC-Na as 1 mM solution in water.

The closest interchromophore distances for the ligands are observed at 12.5 Å, which is outside of the distance for cofacial interchromophore coupling to be observed (Figure 4.16). It is also similar to the distance observed for the structures presented in Chapter III.
Figure 4.16. The configuration of ADCs in **Compounds 4-7** exhibiting large intermolecular distances (12.5 Å) of neighboring cofacial moieties.

Time-resolved emission measurements were conducted to further investigate the local environment of the anthracene units in the structures of **Compounds 4-7** and were compared to that of ADCH₂. Slight variations in the luminescence lifetimes are observed between **Compounds 4-7**. The average lifetime, \( \tau \), is observed to be approximately 1.5 ns. The lifetimes were similar to those observed in early period lanthanide structures in Chapter III. The observed fast component is likely due to the emission from monomeric anthracene moieties, since the lifetimes closely resemble that of anthracene.
(2.0 ns) observed in a monomer arrangement. The observed $\tau_2$ in **Compounds 4-7** are shorter than that observed with ADCH$_2$ because of the increased distance between ADC ligands.

Table 4.6. Photoluminescence lifetimes of **Compounds 4-7** and ADCH$_2$

<table>
<thead>
<tr>
<th>Label</th>
<th>Name</th>
<th>$\tau_1$ (ns)</th>
<th>% comp</th>
<th>$\tau_2$ (ns)</th>
<th>% comp</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADCH$_2$</td>
<td>9,10-anthracenedicarboxylic acid</td>
<td>7.09</td>
<td>74</td>
<td>64.3</td>
<td>26</td>
</tr>
<tr>
<td>Compound 4</td>
<td>Ho-ADC MOF</td>
<td>1.50</td>
<td>76</td>
<td>16.5</td>
<td>24</td>
</tr>
<tr>
<td>Compound 5</td>
<td>Er-ADC MOF</td>
<td>1.48</td>
<td>83</td>
<td>21.2</td>
<td>17</td>
</tr>
<tr>
<td>Compound 6</td>
<td>Tm-ADC MOF</td>
<td>1.79</td>
<td>69</td>
<td>20.5</td>
<td>31</td>
</tr>
<tr>
<td>Compound 7</td>
<td>Yb-ADC MOF</td>
<td>1.32</td>
<td>93</td>
<td>28.0</td>
<td>7</td>
</tr>
</tbody>
</table>
Figure 4.17. Room temperature solid state fluorescence lifetime measurement of Compounds 4-7 and ADCH₂.
4.2.3 Radioluminescence

IBIL was used to probe the fluorescence characteristics of Compounds 4-7 under a 2.5 MeV ionizing proton beam. Compound 5 was the only crystal to produce data during the IBIL experiments. This compound had the largest crystal and face size for the ion beam. The large size allowed the focus beam to readily interface with the crystal surface and not penetrate the crystal during data collection.

The IBIL emission profiles are compared with the photoluminescence spectrum for Compound 5. The Stokes shift observed for the IBIL experiment was large. A pronounced emission profile is observed in the IBIL spectrum of Compound 5 with distinct maxima visible at 475 nm. The similarity of the spectral profiles compared to ADCH$_2$ indicates that the IBIL is a product of the MOF crystal only and not of any ADCH$_2$ impurities from synthesis or a result of damage caused by the beam. The presence of the IBIL spectra validates that the ADCH$_2$ is radioluminescent (scintillating) and that ADC in the MOF structures remain luminescent.
Figure 4.18. IBIL spectrum vs photoluminescence spectrum of Compound 5.

Systematic studies were performed to investigate the effect of beam current on emission decay with Compound 5. Figure 4.18 shows the plotted emission peak profiles with increased PBET for Compound 5. In all cases, the emission intensities decrease with exposure time signifying radiation damage by the proton beam. The radiation damage experiments showed that Compound 5 has a greater capability of resisting radiation damage than ADCH₂ powder. The MOF shows an ability to resist damage up to seven times that of the bulk ligand. Figure 4.19 shows the IBIL fluorescence decay recorded for Compound 5 and ADCH₂ at a beam current of 2.5 MeV with a current density of 12000 nA/cm².
Figure 4.19. a) IBIL spectra of **Compound 5** and b) Intensity vs dose for **Compound 5** and ADCH2.

The decay constants for **Compound 5** and ADCH2 are presented in Table 4.7. The decay constant $D_0$ is high for **Compound 5**, which translates to a high resistance to radiation damage from the 2.5 MeV proton beam.
Table 4.7. Radiation decay constants for ADCH$_2$ ligand and **Compound 5**

<table>
<thead>
<tr>
<th></th>
<th>Current Density (nA/cm$^2$)</th>
<th>Beam Intensity (MeV)</th>
<th>$D_0$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 5</td>
<td>12000</td>
<td>2.5</td>
<td>$7.62 \times 10^{-3}$</td>
<td>0.28</td>
</tr>
<tr>
<td>ADCH$_2$</td>
<td>12000</td>
<td>2.5</td>
<td>$1.51 \times 10^{-3}$</td>
<td>0.33</td>
</tr>
</tbody>
</table>

The spot size of 250 µm x 100 µm was centered unto the crystal under investigation. Flat crystal surfaces were targeted during the IBIL investigations to minimize reflection of ion beam radiation. Figure 4.20 shows a comparison of crystals before and after exposure to the proton beam. Damage to the crystals was readily observed for **Compound 5**, and the MOF crystal shows signs of cracks on the surface with the overall morphology remaining intact.
Figure 4.20. Optical micrographs of a) ADCH$_2$ and b) **Compound 5** at a beam energy of 2.5 MeV, before (left) and after (right) a dose of $3 \times 10^{15}$ /cm$^2$. 
5.0 Introduction

The lanthanide metal series, praseodymium to ytterbium, were explored to coordinate with SDCH$_2$ ligand. The lanthanide metal salts were mixed with SDCH$_2$ in DEF. The metal:ligand ratios explored in MOF synthesis experiments were 1:1, 3:1, and 6:1.

5.1 Experimental Method

**Compound 10** [C$_{64}$H$_{40}$Tm$_3$O$_{24}$]: A mixture of Tm(NO$_3$)$_3$•6 H$_2$O (0.17 mmol, 0.075 g), SDCH$_2$ (0.028 mmol, 0.008 g) and DEF (5 mL) were sealed in an 8 mL scintillation vial and heated to 105°C for 24 h in a conventional oven. The vial was allowed to cool to room temperature and the colorless crystals were filtered and repeatedly washed with fresh DEF under vacuum at room temperature. (Yield = 44%, 0.005 g, based on SDCH$_2$). Elemental Anal. Calcd (%). (FW = 1698.79): C, 50.08; H, 2.87; N,1.57. Found: C, 46.04; H, 2.76; N, 1.11. FTIR (KBr pellet, cm$^{-1}$): 3478br, 3144br, 2981w, 2930w, 2855w, 1684w, 1544w, 1420s, 1101w, 958w, 785m, 707w, 630w, 574w, 526w.

**Compound 11** [C$_{64}$H$_{40}$Er$_3$O$_{24}$]: A mixture of Er(NO$_3$)$_3$•6 H$_2$O (0.084 mmol, 0.037 g), SDCH$_2$ (0.028 mmol, 0.008 g) and DEF (5 mL) were sealed in an 8 mL
scintillation vial and heated to 105°C for 48 hrs in a conventional oven. The vial was allowed to cool to room temperature and the colorless crystals were filtered and repeatedly washed with fresh DEF under vacuum at room temperature. (Yield = 70%, 0.008 g, based on SDCH₂). Elemental Anal. Calcd (%) (FW = 1693.25): C, 50.31; H, 2.88; N, 1.59. Found: C, 46.24; H, 2.86; N, 1.33. FTIR (KBr pellet, cm⁻¹): 3478br, 3144br, 2981w, 2930w, 2855w, 1684w, 1544w, 1420s, 1101w, 958w, 785m, 707w, 630w, 574w, 526w.

5.2. Results and Discussion

5.2.1 Synthesis and Characterization

In most cases (Pr, Nd, Pm, Sm, Eu) no solid products were obtained after several days. In some cases (Tb, Dy, Ho, Yb), solids were obtained, PXRD revealed these to be non-crystalline powders, based on broad, featureless peaks in the diffraction patterns. Crystals were obtained from mixtures containing thulium and erbium only. The PXRD patterns revealed that the two crystalline samples exhibited similar diffraction patterns.

The PXRD patterns of Compounds 10 and 11 along with the simulated pattern of Compound 11 (from SCXA data) are shown in Figure 5.1.
Figure 5.1. PXRD of **Compounds 10** and 11 and simulated diffraction pattern from SCXA data of **Compound 11**.
The diffraction patterns show peaks in identical 2θ positions for the **Compounds 10** and **11** indicating that the crystal structures are isomorphous. The MOFs have identical diffraction patterns to the simulated patterns which suggest the crystal structure remains intact upon vacuum drying. The PXRD patterns of the dried samples are identical to those of the MOF crystals in the original synthesis mixtures, which means removal of uncoordinated solvent at room temperature did not affect the crystal structure. The similarity in the PXRD patterns to that of the SCXA simulated pattern indicates that each sample crystallizes as a pure phase.

SCXA was performed on **Compounds 10** and **11**. Powder X-ray diffraction and elemental analysis were also used to compare **Compounds 10** (Tm-SDC) and **11** (Er-SDC). After data refinement, the best fit data was realized at a space group of C2/c. The single crystal structure parameters for **Compounds 10** and **11** are presented in Table 5.1. It was found that the two materials are isostructural; therefore, structural analysis is detailed for **Compound 11**.
Table 5.1. Crystal structure refinement data for **Compounds 10** and **11**

<table>
<thead>
<tr>
<th></th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>[Tm₃(SDC)₄·6O]</td>
<td>[Er₃(SDC)₄·6O]</td>
</tr>
<tr>
<td>C₆₄H₄₀Tm₃O₂₄</td>
<td></td>
<td>C₆₄H₄₀Er₂O₂₄</td>
</tr>
<tr>
<td>Fw</td>
<td>1698.79</td>
<td>1693.25</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>C₂/c</td>
<td>C₂/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>30.570 (3)</td>
<td>30.678(6)</td>
</tr>
<tr>
<td>b/Å</td>
<td>15.9916 (16)</td>
<td>15.710(3)</td>
</tr>
<tr>
<td>c/Å</td>
<td>25.742 (2)</td>
<td>25.593(5)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>12584 (2)</td>
<td>12335(4)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>D (g/cm³)</td>
<td>0.936</td>
<td>0.898</td>
</tr>
<tr>
<td>μ (1/mm)</td>
<td>2.14</td>
<td>2.062</td>
</tr>
</tbody>
</table>

For **Compound 11**, the crystal structure was refined to a C₂/c space group and monoclinic crystal system. The unit cell dimensions for each crystal are about 31 Å x 16 Å x 25 Å. The volume of the unit cell is 12400 Å³. The calculated densities of the crystals are approximately 0.9 g/cm³, which is considered low density for a MOF.
The MOF is comprised of four SDCH$_2$ ligands for every three lanthanide metals in a unit cell. Unit cell charge is calculated to be ($2^- \times 4 = 8^-$) and is one less than the three trivalent lanthanides ($3^+ \times 3 = 9^+$). This charge imbalance has created an overall charge balance of the MOF to be $1^+$, and coordinating charged solvent must be included to maintain a neutral-balanced framework. So, per asymmetric unit of the MOF, there must be a charge of $1/4^-$ (from $Z = 4$). The identification of the charged species per asymmetric unit could not be solved by crystallography.

Synthesis conditions and the reactants suggest that the charge balance may be from hydrolyzed products DEF molecules (formamide or nitrate ions) in the solution.$^{75}$
Table 5.2 presents the selected bond lengths and bond angles and

Figure 5.2 presents the coordination environment of the Er atoms in Compound 11.

There are four SDC molecules and six oxygen atoms surrounding three Er$^{3+}$ ions per unit cell. There are two crystallographically inequivalent Er$^{3+}$ per unit cell. Seven Er1-O bonds are from the oxygen atoms from six SDC ligands, and one Er1-O bond is from a water molecule.

Table 5.2. Selected bond lengths and bond angles

<table>
<thead>
<tr>
<th></th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er1</td>
<td>O12</td>
<td>2.255(2)</td>
</tr>
<tr>
<td>Er1</td>
<td>O22</td>
<td>2.206(3)</td>
</tr>
<tr>
<td>Er1</td>
<td>O31</td>
<td>2.180(2)</td>
</tr>
<tr>
<td>Er1</td>
<td>O41</td>
<td>2.266(2)</td>
</tr>
<tr>
<td>Er1</td>
<td>O61</td>
<td>2.42(2)</td>
</tr>
<tr>
<td>Er2</td>
<td>O11</td>
<td>2.200(2)</td>
</tr>
<tr>
<td>Er2</td>
<td>O21</td>
<td>2.247(3)</td>
</tr>
<tr>
<td>Er2</td>
<td>O51</td>
<td>2.27(2)</td>
</tr>
<tr>
<td>Er2</td>
<td>O71</td>
<td>2.41(4)</td>
</tr>
</tbody>
</table>
Figure 5.2. Coordination environment of Er1 and Er2 in **Compound 11**. (Hydrogen atoms omitted for clarity).
Four Er2-O bonds are with the oxygen atoms from four SDC ligands, two are with oxygen atoms from an unknown oxygen species, and one is from a water molecule. Er1-O bond lengths range from 2.18 to 2.42 Å. Er2-O bond lengths range from 2.20 to 2.41 Å.

The coordination geometries for both Er$^{3+}$ ions are trigonal prismatic, square faced monocapped with seven coordinating oxygen atoms (Figure 5.3).

Figure 5.3. Er metals present as irregular trigonal prismatic, square faced monocapped polyhedra from Compound 11. (Ligands are removed for clarity).
The SDC ligand is present in one coordination mode. The coordination mode is bridging ($\mu_2:\eta_2$) linking four lanthanide ions (Figure 5.4). The SDC ligand length as an uncoordinated molecule in the solid state is 13.387 Å; however, in this MOF structure the ligand is stretched to 13.537 Å. This is due to the structure being locked between coordinated metals.

![Figure 5.4. SDC in bridging $\mu_2:\eta_2$ coordination mode in Compound 11.](image)

Along the [100] direction, the ligand is connected to Er$^{3+}$ ions in bridging coordination mode (Figure 5.5a). A rhombus-shaped connectivity is observed when the bridging SDC ligands are connected to Er1 ions (Figure 5.5b). Bridging of the metal atoms polyhedra by the ligand’s carboxylates creates undulating chains in [100] direction (Figure 5.5b).

In the [100] direction, bridging SDC creates a 2-D connection with other bridging SDC ligands. Er$^{3+}$ ions are connected through the bridging ($\mu_2:\eta_2$) SDC ligand coordination (Figure 5.6).
Figure 5.5. a) Undulating chains of linked polyhedra in the [100] direction, and b) ligand-metal chain with bridging ADC units in the [001] direction. Hydrogen atoms removed for clarity.
Figure 5.6. Interconnectivity of two bridging chains in **Compound 11**. (Hydrogen atoms and solvent molecules are omitted for clarity).

In the [001] direction, bridging SDC ligands create a diamond-like structure in the framework. The 2-D connectivity (Figure 5.7) and 3-D connectivity (Figure 5.8) is solely based on bridging SDC ligands converging at metal centers.
Figure 5.7. Interconnectivity of bridging ligand chains in Compound 11. (Hydrogen atoms and solvent molecules are omitted for clarity).
Figure 5.8. 3-D crystal structure packing along the [001] axis of Compound 11. (Uncoordinated solvent was omitted for clarity).
Simplifying the structure using TOPOS software reveals a network topology structure with the Er atoms and the ligands as nodes (Figure 5.9). To derive the net structure, the SDC ligands are reduced to 4-coordinate blue nodes representing the bridging coordination mode. The Er1 ion is shown as a 6-connecting pink node, and Er2 ion is shown as a 4-connecting pink node (Figure 5.9). In the [001] direction, the pores are observed in the MOF, resembling a “chain-linked fence”. 46,75

Figure 5.9. Topology net of Compound 11 viewed along the [001] direction. (Solvent molecules are removed for clarity)

Figure 5.10 presents the solvent accessible voids that are observed for this porous MOF. The pore dimensions were calculated using TOPOS software at 15.40 Å x 27.27 Å. These dimensions have created large solvent accessible voids, at approximately 442.02 Å². The pattern is shown when viewed along the [100] direction (Figure 5.10a) and the rhombus voids are observed along the [001] direction (Figure 5.10b).
Figure 5.10. Solvent accessible voids for **Compound 11** viewed along the a) [100] direction and b) space-filling model in the [001] direction.
The FTIR spectra for **Compounds 10, 11** and SDCH\textsubscript{2} powder are presented in Figure 5.11. The band at 3478 cm\textsuperscript{-1} indicates the presence of OH as adsorbed water species on the MOFs and SDCH\textsubscript{2} powder. The bands at 3144 cm\textsuperscript{-1} and 2981 cm\textsuperscript{-1} observed with the SDCH\textsubscript{2} ligand indicate aromatic C-C stretching. The band observed at 1681 cm\textsuperscript{-1} for SDCH\textsubscript{2} indicates the highly protonated carboxylic acid functional group. This band is not observed for **Compounds 10** and **11**, instead bands at 1670 cm\textsuperscript{-1} and 1600 cm\textsuperscript{-1} are observed indicating deprotonated carboxylic acid functional groups. The band at 1420 cm\textsuperscript{-1} is consistently observed throughout MOFs and SDCH\textsubscript{2} which are the aromatic moieties. The band at 1290 cm\textsuperscript{-1} for SDCH\textsubscript{2} indicates C-O bending, which is absent in **Compounds 10** and **11**. The ligands that are locked in position in the MOF do not allow much movement of the C-O bond of the carboxylic acid.
Figure 5.11. FTIR spectra of **Compounds 10** and 11 and SDCH$_2$ at room temperature.
The samples were subjected to a post synthesis chloroform exchange procedure to remove excess uncoordinated solvents from MOF structure. TGA was performed under a steady flow of nitrogen.

Table 5.3 displays the thermal weight loss events, and molecular assignments for **Compounds 10 and 11.** The observed weight loss can be attributed to the degradation of MOF moieties with increasing temperature.

<table>
<thead>
<tr>
<th>Event temp (°C)</th>
<th>Wt. loss (%)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 - 90</td>
<td>5</td>
<td>Adsorbed H₂O, CHCl₃</td>
</tr>
<tr>
<td>90 - 200</td>
<td>10</td>
<td>Uncoordinated DEF</td>
</tr>
<tr>
<td>550-600</td>
<td>20</td>
<td>SDC decomposition</td>
</tr>
<tr>
<td>600-900</td>
<td>10</td>
<td>Metal oxide residue (remaining)</td>
</tr>
<tr>
<td>Compound 11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 - 90</td>
<td>10</td>
<td>Adsorbed H₂O, CHCl₃</td>
</tr>
<tr>
<td>90 - 200</td>
<td>10</td>
<td>Uncoordinated DEF</td>
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<tr>
<td>550-600</td>
<td>20</td>
<td>SDC decomposition</td>
</tr>
<tr>
<td>600-900</td>
<td>10</td>
<td>Metal oxide (remaining)</td>
</tr>
</tbody>
</table>

In general, the TGAs of the samples depicted in Figure 5.12 show small events at approximately 200 °C, with 25% weight loss due to DEF and CHCl₃. Major degradation events at approximately 550°C of about 15% weight loss are attributed to degradation and loss of SDC. Residues of approximately 25% weight are attributed to the metal oxide.
Figure 5.12. TGA curves for **Compounds 10** and **11**.
5.2.2 Photoluminescence

The photoluminescence spectra of Compounds 10 and 11 and SDCH$_2$ are presented in Figure 5.13. The excitation and emission spectra are similar to those reported for SDCH$_2$. As for SDCH$_2$ powder, Compounds 10 and 11 show excitation peaks in the 350 to 450 nm region. The emission peaks observed in Compounds 10 and 11 are therefore SDC linker-based. As for SDCH$_2$, the spectra of Compounds 10 and 11 show Stokes shifts (Table 5.4). Stokes shifts are due to non-radiative pathways in the structures. Compound 10 displays the smallest Stokes shift at 41 nm compared to Compound 11 and SDCH$_2$. 

![Photoluminescence spectra](image)
Figure 5.13. Photoluminescence spectra for **Compounds 10 and 11** with SDCH$_2$ shown as a), b), and c), respectively.
Table 5.4. Stokes shifts for **Compounds 10, 11** and SDCH$_2$

| Sample                        | Stokes Shift || Stokes Shift |
|------------------------------|---------------|---------------|
|                              | Ex (nm)-Em    | (nm)          |
| (Compound 10) Tm-SDC         | 41            |
| (Compound 11) Er-SDC         | 50            |
| SDCH$_2$                     | 80            |

Figure 5.14 shows an overlay of the emission spectral profiles of **Compounds 10, 11, SDCH$_2$, and SDC-Na** in solution. The powdered solid SDCH$_2$ luminescence spectrum is a broad featureless peak at 470 nm. The SDCH$_2$ powder is in a dense stilbene arrangement, which increases interactions and shortens $\pi$-$\pi$ distances between aromatic faces of the stilbene moiety. Hydrogen bonding between terminal carboxylic acid groups introduces short interchromophore stacking distances as in edge-to-face solid packing structures.$^{44}$

SDC-Na represents interchromophore coupling at its minimum and molecular spacing at its maximum; it has the highest energy for its $\pi^*\rightarrow\pi$ transitions. Its spectrum matches that of the monomeric stilbene emission spectra reported by Bauer et al.$^{30}$ This is ascribed to the fact that the SDC units that are further apart have less distribution of the non-radiative relaxation pathways, hence increasing the extent of higher energy electronic transitions.

**Compounds 10 and 11** exhibit $\lambda_{\text{max}}$ between ADC-Na and SDCH$_2$. The peaks observed and their associated vibronic transitions are presented in Table 5.5. Within a MOF, the spacing between ligands is fixed. The changes in the spectral profile are not
due to the framework, but due to the charge transfer through the metals to neighboring chromophores. Since the ligands are in an ordered, fixed orientation throughout the crystal, a more narrow distribution of vibronic level populations is observed (Figure 5.15).

The $\lambda_{\text{max}}$ for **Compound 10** is blue-shifted from that of SDCH$_2$ (470 nm) to 425 nm. The peak profile is similar to that of SDC-Na in solution. This is due to limited interchromophore coupling due to rigid ligand spacing in the structure. Measured distances of neighboring sets of SDCH$_2$ linkers are $\sim$6.65 Å (Figure 5.15), which is in the intermediate range for similar structures and for interchromophore coupling (4-8 Å).$^{30}$

The $\lambda_{\text{max}}$ for **Compound 11** is blue-shifted from that of SDCH$_2$ (470 nm) to 440 nm. The peak profile is broader than that observed for **Compound 10**. It is uncertain as to why this phenomenon is observed, but may be due to the Er$^{3+}$ ion during luminescence.
Figure 5.14. Comparison of normalized emission data of Compound 10 and 11 (crystal) and SDCH₂ (powder) with trans-4,4’-stilbene dicarboxylate sodium salt in water (SDC-Na) after excitation λ = 330 nm.

Table 5.5. Wavelength position associated with vibronic state transitions

<table>
<thead>
<tr>
<th>Emission Transition</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1,0 → S0,0</td>
<td>416</td>
</tr>
<tr>
<td>S1,0 → S0,1</td>
<td>440</td>
</tr>
<tr>
<td>S1,0 → S0,2</td>
<td>464</td>
</tr>
<tr>
<td>S1,0 → S0,3</td>
<td>496</td>
</tr>
</tbody>
</table>
Figure 5.15. Space filling model of cofacial SDC positions in **Compounds 10 and 11** at a distance of 6.65 Å.
Time-resolved emission measurements were used to further investigate the local environment of the stilbene units in the crystal structures of **Compounds 10, 11** and, were compared to that of SDCH$_2$. The intensity vs. time decay curves for **Compounds 10, 11**, and SDCH$_2$ are presented in Figure 5.16. The fluorescence lifetimes are presented in Table 5.6. The radiative lifetime for a solid stilbene crystal is estimated to be 1.7 ns and becomes shortened to around 100 ps in solution at room temperature.$^{44}$ The major factor contributing to a reduced lifetime is the *trans-cis* isomerization. Fluorescence lifetimes are slowest (0.76 ns) for the SDCH$_2$ standard because of the close edge-to-face packing arrangement of the ligands, which facilitates alternate pathways during emission along with the increased interchromophore coupling.$^{44}$

**Compounds 10** and **11** exhibit lifetimes of $\tau_1 = 0.41$ and 0.36, respectively. This is faster than that of SDCH$_2$, and are within range for reported stilbene crystals.$^{44}$ The observed fast component are due to the emission from monomeric stilbene moieties, since the lifetimes are faster than that of stilbene in a powdered solid.
Figure 5.16. Solid state fluorescence lifetime measurements of Compounds 10 and 11 and SDCH₂. Collections performed at room temperature (λ<sub>ext</sub> = 341 nm).

The similarity in lifetimes are consistent with similarity in the isostructural arrangement of SDC in the MOFs. A faster lifetime is observed for the MOFs compared with SDCH₂ ligand, and is consistent with the limited amount of non-radiative transitions that occur with the highly spaced ligands. The lifetime of the longer-lived component, τ₂, is also attributed to the interchromophore distances, for SDCH₂ powders τ₂ is 1.7 ns. The
τ₂ of **Compounds 10** and 11 are 1.71 and 3.36 ns, respectively. The observed τ₂ in **Compounds 10** and 11 are similar to the values observed for SDCH₂, therefore indicating that packing arrangement has no direct influence on the longer lifetime component.

A decrease in photoluminescence lifetime is suggested to correlate with an increased quantum efficiency for that transition.⁴⁴

### Table 5.6. **Compounds 10, 11** and SDCH₂ fluorescence lifetime decay data

<table>
<thead>
<tr>
<th>Label</th>
<th>Name</th>
<th>τ₁ (ns)</th>
<th>% comp</th>
<th>τ₂ (ns)</th>
<th>% comp</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDCH₂</td>
<td>4,4'-stilbenedicarboxylic acid</td>
<td>0.764</td>
<td>93</td>
<td>1.70</td>
<td>7</td>
</tr>
<tr>
<td>Compound 10</td>
<td>Tm-SDC MOF</td>
<td>0.408</td>
<td>89</td>
<td>1.71</td>
<td>11</td>
</tr>
<tr>
<td>Compound 11</td>
<td>Er-SDC MOF</td>
<td>0.362</td>
<td>91</td>
<td>3.36</td>
<td>9</td>
</tr>
</tbody>
</table>

#### 5.2.3 Radioluminescence

IBIL was used to probe the radioluminescence characteristics of **Compounds 10** under a 1.5 and 2.5 MeV ionizing proton beam. IBIL spectra were collected on a CCD Spectrophotometer, and the emission decays were observed after the crystals were exposed to the proton beam. **Compound 10** was used for the majority of the investigations because of the collected emission data and its large 240 μm size.

The IBIL emission profiles are compared with the photoluminescence spectra of **Compound 10** and SDCH₂ (Figure 5.17). A pronounced emission profile is observed in the IBIL spectra of **Compound 10** and SDCH₂ with distinct maxima visible at 525 and 490 nm, respectively. **Compound 10** when exposed to the 1.5 MeV exhibits a large
Stokes shift between the IBIL emission and PL spectra. The change in emission spectra indicates structural damage as it relates to the distances between chromophores. At 2.5 MeV, the shift between PL and IBIL decreases, indicating that less damage is experienced by the MOF (Figure 5.17). Furthermore, a broader peak is observed for the 1.5 MeV beam than the 2.5 MeV beam, indicating a larger distribution of radiative pathways due to close ligand packing after structure damage.

The similarity of the spectral profiles compared to SDCH₂ shows that the IBIL is a product of the MOF crystal only and not of any SDCH₂ impurities from synthesis or a result of damage caused by the beam. The presence of the IBIL spectra validates that the SDCH₂ is radioluminescent (scintillating) and that SDC in the MOF structures remain luminescent.

![Graph of normalized intensity vs. wavelength](image)

- (SDCH₂) Ex_475
- (SDCH₂) Em_341
- (SDCH₂) IBIL
Figure 5.17. IBIL excitation and emission spectra of Compound 10 and SDCH₂.

The SDCH₂ standard shows little shift between PL and IBIL spectra, which indicates little structure change upon ionization. The ligand emission is of a low energy in this solid powder because of the chromophore distances, thus packing is not affected by the ion beam radiation. However, the emission peak’s spectral profile becomes more evenly
distributed, signifying a more even distribution of radiative pathways. The Stokes shifts for the SDCH$_2$ standard and **Compound 10** at 1.5 MeV and 2.5 MeV are presented in Table 5.7.

For practical scintillator use, the IBIL spectra of **Compound 10** from beam energy of 2.5 MeV is comparable to their observed photoluminescence phenomena, indicating minimal structural damage by the radioluminescent material.

Table 5.7. Observed IBIL Stoke shifts for **Compound 10** and SDCH$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ex (nm)-Em (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Compound 10) 1.5 MeV Tm-SDC</td>
<td>116</td>
</tr>
<tr>
<td>(Compound 10) 2.5 MeV Tm-SDC</td>
<td>71</td>
</tr>
<tr>
<td>2.5 MeV SDCH$_2$</td>
<td>80</td>
</tr>
</tbody>
</table>

Radioluminescence lifetime measurements were carried out for **Compound 10** and SDCH$_2$. Shorter scintillation lifetimes are observed for **Compound 10** (1.2 ns) vs. SDCH$_2$ (2.0 ns), which is consistent with the photoluminescent lifetimes measured previously (Figure 5.18). The samples were exposed to $^{137}$Cs ionizing radiation ($\gamma$ radiation) under experimental conditions described in Chapter III. The intensity vs. time decay curves are presented in Figure 5.20. The data were fitted to a biexponential function with Equation 3. Radioluminescence lifetime measurements show that the major components of scintillation lifetime are approximately 2 ns longer compared to its fluorescence lifetime (0.4 ns). Ion recombination phenomenon, which involves the
recombining of electrons and their secondary electrons, extends the time for the subsequent emission transitions processes.\textsuperscript{5}

Figure 5.18. Scintillation lifetime studies of \textbf{Compound 10} and SDCH\textsubscript{2} at room temperature using TCSPC including a model fit.
Studies were performed to investigate the effect of beam current density and radiation dosage on emission decay for **Compound 10**. The emission peak profiles are plotted in Figure 5.19. Decrease in fluorescence activity is observed with increase in proton beam exposure time (PBET).
Figure 5.19. Representative dose-dependent IBIL spectra demonstrating intensity decay for 1.5 and 2.5 MeV for a) Compound 10 and b) SDCH₂.

The maximum IBIL intensity for **Compound 10** and SDCH₂ were used to compare the rate of intensity degradation with radiation dose. Notably, the intensities
decrease as the exposure to the proton beam increases for the MOF and the SDCH₂ standard. A peak shift is noticeable for Compound 10 after exposure to the beam, and suggests damage after exposure. A less noticeable emission shift is observed for the SDCH₂ standard, which supports the idea of little change in the immediate environment upon heating and irradiation.
Figure 5.20. Normalized intensities of dose-dependent IBIL spectra for Compound 10 and SDCH₂ crystal, with 12000 nA/cm² beam current at different beam energies.
The decay constants determined from these experiments (Table 5.8) suggests that the MOF crystal is slightly more resistant to radiation damage than SDCH₂ powder. Decay constant $D_0$ refers to the ability of the sample to resist radiation, the higher number meaning more resistance. The $\beta$ factor correlates to the dispersion of the data points used in the calculation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Current Density (nA/cm²)</th>
<th>Beam Intensity (MeV)</th>
<th>$D_0$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 10</td>
<td>12000</td>
<td>2.5</td>
<td>$4.22 \times 10^{-1}$</td>
<td>0.889</td>
</tr>
<tr>
<td>(Tm-SDC)</td>
<td>12000</td>
<td>1.5</td>
<td>$1.86 \times 10^{-2}$</td>
<td>0.137</td>
</tr>
<tr>
<td>SDCH₂</td>
<td>12000</td>
<td>2.5</td>
<td>$1.16 \times 10^{-5}$</td>
<td>0.156</td>
</tr>
<tr>
<td></td>
<td>12000</td>
<td>1.5</td>
<td>$7.57 \times 10^{-4}$</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The radiation tolerance of the MOF is higher than of the SDCH₂ powder because of the locked orientation of the SDC ligands. The decrease in light output in the MOF is less drastic than that observed for the SDCH₂ powder. However, the peak position changes after ion beam exposure indicating MOF structural damage. The SDCH₂ spectra maxima did not shift after ion beam exposure.

The spot size of 250 µm x 100 µm was centered on the crystal under investigation. Flat crystal surfaces were targeted during the IBIL investigations to minimize reflection of ion beam radiation. Figure 5.21 shows a comparison of crystals before and after exposure of the proton beam.
Figure 5.21. Optical micrographs of **Compound 10** before (left) and after (right) exposure to 2.5 MeV proton dose of $1.19 \times 10^{15}$/cm$^2$, red arrows pointing to spots to identify ion beam damage.
Figure 5.22. Optical micrographs of **Compound 10** before (left) and after (right) exposure to 1.5 MeV proton dose of $3.00 \times 10^{15}$/cm$^2$, with red arrows pointing to spots to identify possible ion beam damage.
CHAPTER VI
CONCLUSION

This research explored the synthesis of anthracene and stilbene based metal-organic framework (MOF) structures as potential scintillating (radioluminescent) materials for use in the detection of gamma radiation. The dicarboxylic acid derivative, 9,10-anthracenedicarboxylic acid (ADCH$_2$) and trans-4,4’-stilbenedicarboxylic acid (SDCH$_2$) of each organic molecule was used as the linker, in combination with a range of lanthanide metal ions, to synthesize new 3-D MOF structures under hydrothermal conditions.

The ADC-MOFs show linker-based photoluminescence properties with more defined vibronic peaks in their emission profile and their emission ($\lambda_{\text{max}} \sim 435$ nm) blue shifting from that of the ADCH$_2$ powder ($\sim 500$ nm) and closer to the organic molecule in monomer arrangement ($\lambda_{\text{max}} \sim 420$ nm). The structures also show photoluminescence lifetimes of 1.3 ns to 2.0 ns, which is similar to the reported value for monomeric anthracene units.

The blue-shift and reduction in lifetime are indicative of the isolation of the ligand units within the MOF structure which minimizes $\pi-\pi$ interactions between the aromatic moieties, and also reduces the occurrence of dimerization between anthracene units,
thereby limiting the non-radiative relaxation pathways. On exposure to ionizing radiation (protons and γ-rays), the ADC-MOFs demonstrated scintillation properties with emission profiles that are similar to those observed in photoluminescence, but with radioluminescence lifetime of ~ 6 ns, which is similar to that of the ADCH₂ powder.

A combination of SDCH₂ and the lanthanide metals, produced two isostructured MOFs, containing Tm³⁺ and Er³⁺, under the hydrothermal synthesis conditions. The 3-D structure contained ultra large diamond-shaped pores with dimensions of 16 Å x 30 Å. Like the ADC-MOF structures, linker-based luminescence was observed during photoluminescence. A blue-shift was observed for the SDC-MOF structures ($\lambda_{\text{max}} \sim 425$ nm) compared to that of bulk SDCH₂ ($\lambda_{\text{max}} \sim 475$ nm). This closely resembles that of the monomeric isolation of SDC ($\lambda_{\text{max}} \sim 475$ nm). Their photoluminescence lifetime is ~0.76 ns, about half of that for observed SDCH₂ powder. The blue shift and reduction in lifetime is attributed to the limited ability for SDC π-π interactions, thus minimizing associated non-radiative relaxation pathways.

The objective of isolating anthracene and stilbene in a MOF was achieved. Their isolation has the potential to improve their performance as scintillators.
APPENDIX A

SUPPORTING INFORMATION

Figure AA 1. Scanning Electron Microscopy (SEM) images of Compound 10.

Figure AA 2. SEM images of Compound 11.
Figure AA 3. SEM of a) Compound 2 and b) Compound 4.  
IBIL Control Data
Figure AA 4. Carbon tape background analysis at a) 1.5 and b) 2.5 MeV
Figure AA 5. Faraday Cup In lights a) on and b) off experiments for background information on zero beam interaction with sample stage.
Figure AA 6. Exact spot size (rectangle) of focused ion beam onto YAG crystal. Photo taken from under the YAG crystal, with measuring image. Ion beam spot size estimated at 120 μm x 175 μm. Image aspect ratios are kept consistent.
Figure AA 7. YAG fluorescence spectra collected during ion beam exposure. Maximum sensitivity of the spectrophotometer is observed.
Figure AA 8. Sample stage used for the IBIL experiments. Sample stage under a constant $4.0 \times 10^{-7}$ Torr vacuum pressure.
REFERENCES

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