Metal-mediated reactivity in the organic solid state: from self-assembled complexes to metal–organic frameworks

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Received (in Cambridge, UK) 4th April 2007
First published as an Advance Article on the web 8th May 2007
DOI: 10.1039/b516074j

The purpose of this *tutorial review* is to address the use of metal ions to mediate reactions in the organic solid state. We describe metal complexes and coordination networks that facilitate dimerizations, oligomerizations and polymerizations of olefins and acetylenes *via* irradiation (*e.g.* ultraviolet (UV) and ^{60}Co γ-rays) and thermal annealing. We show how metal ions can be utilized to direct the formation of polymers and molecules. We also describe how supramolecular chemistry has recently influenced dimerization processes in self-assembled metal–organic solids.

1 Introduction

Reactions conducted in the organic solid state provide a remarkable opportunity to synthesize materials and molecular compounds that are less available, or unavailable, in solution.[1] Unfortunately, the sensitivity of solid-state structure to molecular structure makes it difficult to control reactivity in the solid state, owing to structure demands of close packing.[2] As a result, many attempts to control reactions in the organic solid state have been largely based on trial and error.[3] This means that the goal of solid-state chemists to synthesize reactive molecular materials with desired physical and chemical properties has remained a difficult challenge.

In recent years, the fields of crystal engineering[4] and supramolecular chemistry[5] have emerged as useful tools to control reactions in solids. Noncovalent bonds such as hydrogen bonds, coordination bonds, π–π stacking, and halogen–halogen forces have been exploited to organize reactants in geometries suitable for reaction.[6] In this context, coordination bonds coupled with principles of self-assembly have been recently employed to direct organic solid-state reactivity.[7] The major focus has been to design and construct metal complexes with precise architecture, containing unsaturated reactive centers (*e.g.* alkenes, alkynes) that form new covalent bonds upon irradiation or thermal annealing. A recent focus in this regard has been the [2 + 2] photodimerization.[8] The detailed geometry criteria for the reaction follow the topochemical postulate outlined by Schmidt and Cohen.[9] Thus, a [2 + 2] photodimerization will typically occur in the solid state if the reactive centers are aligned parallel and separated by less than 4.2 Å. Products of metal-mediated reactions in the solid state have included polymers, oligomers, and molecules. This review aims to present the basic principles behind metal-mediated solid-state reactivity with a view on the role of metal ions and coordination-driven self-assembly to design and construct reactive solids.

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2 Solid-state reactions controlled by metal ions

As stated, metal ions can be used to form molecules, oligomers, and/or polymers in the crystalline state. We will first outline how metal ions have been employed to direct the formation of polymers and oligomers. We will then move to dimerizations, an area that has been particularly influenced by the field of supramolecular chemistry.

2.1 Polymerizations

Metal-mediated solid-state reactions that produce polymers were initially encountered in metal salts containing carboxylate ions as ligands (Table 1).

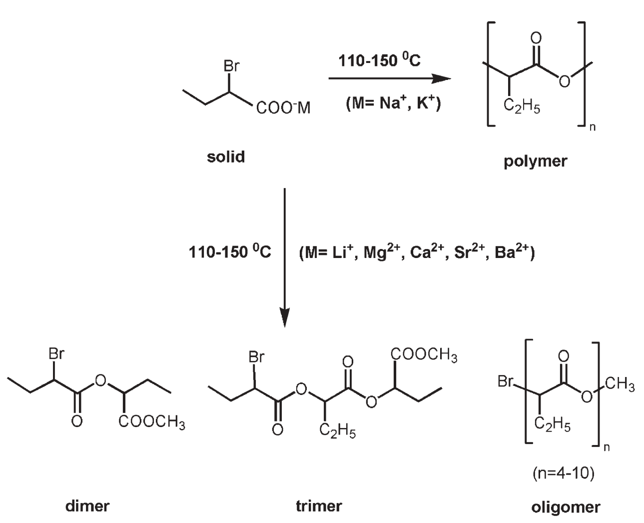
Although the investigation of metal-mediated solid-state polymerizations dates back to the early work of Bischoff,[10] Bezzi,[11] Asahara,[12] Davidov,[13] and Morawetz,[14] it is only in the past 20 years that the use of metal ions to engineer the orientation of reactants in crystal lattices to form polymers has been studied in great detail. In particular, extensive work by Foxman and co-workers has described the design and discovery of reactive solids that lead to the formation of polymers based on controlling metal size and crystal architecture. Metals typically self-assemble with the organic ligands to form two-dimensional (2D) coordination polymers with close packing of the reactants and a short distance between the reactive centers. Polymers have formed from bilayer packing motifs with reactive groups typically at distances of less then 4.2 Å. UV- or ^{60}Co γ-ray radiation, as well as heating, have led to the formation of covalent bonds between the reactive centers to give the polymers.

2.1.1 Metal alkanoates and related systems. Pioneering studies on thermal reactivity of alkali and alkaline earth halogenated alkanoates were carried out by Bischoff and Walden about 120 years ago[10] and extended by Bezzi[11] and

Table 1 Solid-state polymerization reactions mediated by metal ions

Compound	Method	Yield^a (%)	Ref.
Na-BrBA	Thermal annealing (110–150 °C)	95	15
K-BrBA	Thermal annealing (110–150 °C)	78	15
Na-BrPA	Thermal annealing (120–150 °C)	90	16
K-BrPA	Thermal annealing (120–150 °C)	84	16
Na-ClPA	Thermal annealing (120–150 °C)	90	16
Li-3-BMBA	Thermal annealing (120–150 °C)	20	17
Na-3-BMBA	Thermal annealing (140–160 °C)	84	17
K-3-BMBA	Thermal annealing (140–150 °C)	94	17
Na-4-BMBA	Thermal annealing (220–240 °C)	99	17
K-4-BMBA	Thermal annealing (220–240 °C)	97	17
Na-4-BMPAA	Thermal annealing (140–160 °C)	85	17
K-4-BMPAA	Thermal annealing (130–160 °C)	98	17
LI-4-BEBA	Thermal annealing (160–180 °C)	34	18
Na-4-BEBA	Thermal annealing (160–180 °C)	75	18
K-4-BEBA	Thermal annealing (160–180 °C)	77	18
LiA^b	^{60}Co γ-ray irradiation (0.2 Mrad)	20	14
NaA	^{60}Co γ-ray irradiation (0.2 Mrad)	12	14
KA	^{60}Co γ-ray irradiation (0.8 Mrad)	34	14
CaA	^{60}Co γ-ray irradiation (0.9 Mrad)	78^a	20
LiMA^c	Thermal annealing (200–250 °C)	62	21
NaMA	^{60}Co γ-ray irradiation (0.2 Mrad)	7	14
	Thermal annealing (200–250 °C)	8	21
KMA	^{60}Co γ-ray irradiation (0.8 Mrad)	3	14
	Thermal annealing (200–250 °C)	4	21
ZnMA	^{60}Co γ-ray irradiation (1 Mrad)	90^a	20
	Thermal annealing (200–250 °C)	23	21
BaMA	^{60}Co γ-ray irradiation (0.3 Mrad)	93^a	20
	Thermal annealing (200–250 °C)	67	21
Li-4-VBA	Thermal annealing (240–280 °C)	9	22
Na-4-VBA	Thermal annealing (240–280 °C)	53	22
K-4-VBA	Thermal annealing (240–280 °C)	74	22
Mg-4-VBA	Thermal annealing (260–280 °C)	25	22
Ca-4-VBA	Thermal annealing (260–280 °C)	9	22
Sr-4-VBA	Thermal annealing (260–280 °C)	6	22
Ba-4-VBA	Thermal annealing (260–280 °C)	3	22
α-Co(4-Vpy)$_2$Cl$_2$	Thermal annealing (105–130 °C)	94	23
α -Zn(4-Vpy)$_2$Cl$_2$	Thermal annealing (115–130 °C)	Not reported	23
Cu(4-Vpy)$_2$Cl$_2$	Thermal annealing (115–130 °C)	Not reported	23
Ni(4-Vpy)$_2$Cl$_2$	Thermal annealing (115–130 °C)	Not reported	23
$Ca(CH_2{=}CHCH_2CO_2)_2\cdot H_2O$	^{60}Co γ-ray irradiation (305 kGy dose)	97	24
$Na(O_2CC{\equiv}CH)$	^{60}Co γ-ray irradiation (872 kGy dose)	75	26
$(CH_3)_2Tl(O_2CC{\equiv}CH)$	^{60}Co γ-ray irradiation (33.7 Mrad), X-rays	26	27
$Mg(O_2CC{\equiv}CH)_2(OH_2)_2$	^{60}Co γ-ray irradiation (48.3 Mrad), X-rays	22	28
$Sc(O_2CC{\equiv}CH)$	^{60}Co γ-ray irradiation (40 Mrad)	55	29
$La_2(O_2CC{\equiv}CH)_6(H_2O)_4\cdot 2H_2O$	^{60}Co γ-ray irradiation (65.1 Mrad)	59	30
$[Cd(ADC)(H_2O)_3]$	Thermal annealing (160 °C)	Not reported	31
$[Ln_2(ADC)_3(H_2O)_6]\cdot 2H_2O$	Thermal annealing (>150 °C)	Not reported	31

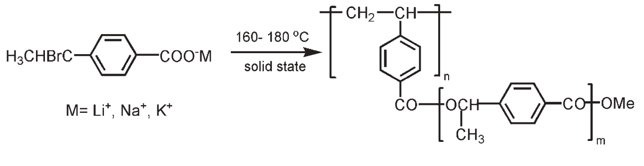
^{a} Yields corresponds to the maximum reported yield. ^{b} A = acrylate. ^{c} MA = metal acrylate.



Scheme 1

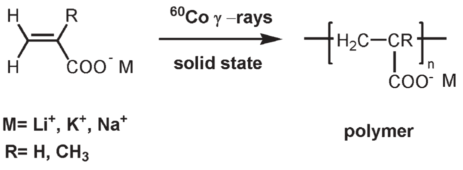
Asahara *et al.*[12] in the 1950s. Although the identities of the products were not reported, these early investigations led to more detailed comprehensive studies. In particular, Naruchi and co-workers reported, in the 1980s, thermal reactions of salts of 2-bromo-*n*-butyric acid (BrBA) with alkali and alkaline earth metals (*e.g.* Li, Na, K, Mg, Ca, Ba and Sr).[15] The Na-BrBA and K-BrBA solids exhibited high reactivity, forming poly(2-hydroxybutyrate) (M_w = 1000–3500 Da) in up to 95% yield (Scheme 1). The Li$^+$, Mg^{2+}, Ca^{2+}, Ba^{2+} and Sr^{2+} salts produced mixtures of dimers, trimers and oligomers, which was attributed to the formation of amorphous monomeric salts.

In a related study, Naruchi and co-workers demonstrated that upon heating, alkali and alkaline earth salts of 2-bromopropanoic acid (BrPA) and 2-chloropropanoic acid (ClPA) led to the formation of poly(lactic acid) and oligo(lactic acid), as well as dimers and trimers.[16] Polyesters were also produced when salts of halogenated aromatic carboxylic acids such as *n*-bromomethylbenzoic acid (BMBA) (where *n* = 3, 4) and (4-bromomethylphenyl)acetic acid (BMPAA) with alkali metals underwent polycondensations upon heating.[17] In contrast, thermal reactions of salts of 4-(1-bromoethyl)benzoic (4-BEBA) acids (4-BEBA) with alkali metals (*e.g.* Na$^+$, Li$^+$, K$^+$) led to oligocondensation of carboxylates with bromides, as well as vinyl polymerization forming the unexpected graft copolymer poly(4-vinylbenzoate)-*graft*-oligo(oxycarbonyl-1,4-phenylenethylidine) in up to 77% yield (Scheme 2).[18,19]



Scheme 2

2.1.2 Metal alkenoates and related systems. In the late 1950s, Morawetz and Rubin studied the ^{60}Co γ-ray induced solid-state polymerizations of various metal acrylates and methacrylates containing K$^+$, Li$^+$ and Na$^+$ ions (Scheme 3).[14] Analyses of the course of the solid-state polymerizations revealed that the acrylates were much more reactive compared to the methacrylates. In addition, K$^+$ acrylate was shown to polymerize at a much higher rate compared to Na$^+$ or Li$^+$, leading to the formation of high molecular weight atactic polyacrylates (M_w = 100 000–400 000 Da) in up to 34% yield. For the methacrylates, the order of reactivity was reversed, with Na$^+$ methacrylates showing a higher reactivity compared to the K$^+$ and Li$^+$ salts. Although the lack of comprehensive crystal structure data prevented a detailed explanation of the rationale behind the reactivity, it was suggested that the reactivity was controlled by the geometry of the crystal lattice. Later, ^{60}Co γ-ray induced solid-state polymerizations of various phases of Ca^{2+} acrylates, as well as Ba^{2+} and Zn^{2+} methacrylates were reported.[20]



Scheme 3

Naruchi and co-workers have investigated the thermal reactivity of alkali and Zn^{2+} salts of methacrylic acid.[21] It was shown that upon heating in the temperature range of 200–250 °C, alkali (*e.g.* Li$^+$, Na$^+$, K$^+$) and Zn^{2+} methacrylates produced high molecular weight polymers. Lithium methacrylate was most reactive, leading to the formation of high molecular weight polymethacrylate in up to 62% yield. In the late 1990s, Naruchi and co-workers also described the thermal polymerization of alkali and alkaline earth salts of 4-vinylbenzoic acid.[22]

Agnew and Brown, in the 1970s, investigated the solid-state polymerizations of 2- and 4-vinylpyridine (Vpy) complexes of divalent cobalt, nickel, copper and zinc chlorides.[23] Single crystals of α-Co(4-Vpy)$_2$Cl$_2$ polymerized to produce high-molecular weight (M_w = 60 000 Da) head-to-tail polyvinylpyridines when heated in the temperature range 105–130 °C. A maximum yield of 94% was reported. α-Zn(4-Vpy)$_2$Cl$_2$, which was isomorphous to α-Co(4-Vpy)$_2$Cl$_2$, also produced high molecular weight head-to-tail polymers upon extended heating at 115–120 °C. Thermal polymerization of Cu(4-Vpy)$_2$Cl$_2$ and Ni(4-Vpy)$_2$Cl$_2$ proceeded with difficulty, which was attributed to tight packing and small thermal motion in the crystal lattice. Polymerization was not observed with the remaining solids owing to the coordination complexes decomposing upon heating. Ultraviolet, γ-ray, or sunlight irradiation of the vinylpyridine salts also failed to produce polymerized products.

Beginning in the 1990s, Foxman and co-workers investigated the solid-state reactivity of a series of metal alkenoates based on unsaturated carboxylates substituted at different positions.[7] Among the carboxylates studied, aquabis(3-butenoato)calcium led to the formation of a polymerized product.[24] X-Ray crystal structure analysis of the salt revealed the formation of a 2D coordination polymer with a bilayer structure motif (Fig. 1). The alkene moieties formed infinite chains aligned parallel with short –C=C···C=C– contacts (3.73–3.90 Å). ^{60}Co γ-ray radiation was used to induce the

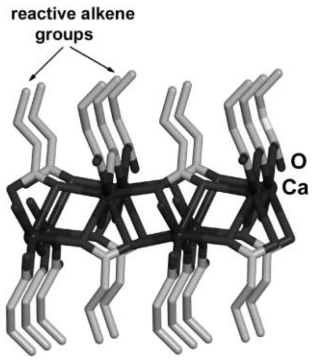


Fig. 1 Crystal structure of aquabis(3-butenoato)calcium representing the parallel alignment of the alkenes. Hydrogen atoms omitted for clarity.

polymerization and led to high molecular weight polymer (M_w = 400 000 Da) in up to 97% yield.

2.1.3 Metal alkynoates and related systems. In the 1960s, Davidov and co-workers reported the first study of the solid-state reactivities of metal alkynoates. It was shown that upon γ-irradiation, alkali and alkaline earth metal propynoates underwent solid-state polymerization that led to the formation of the corresponding polypropynoates in up to 84% yield.[13] However, the structures of the polypropynoates were not fully determined.

Based on these investigations, and using the topochemical postulate of Schmidt as a starting point, Foxman and co-workers initiated a series of comprehensive and systematic studies on the solid state reactivities of metal alkynoates.[25] The studies, which began in the 1980s, described a series of metal alkynoates with remarkable reactivities. In particular, Foxman and co-workers demonstrated that metal alkynoates (*e.g.* Na^+, Zn^{2+}, Cu^{2+}, Mg^{2+}, Sc^{3+}, Tl^{3+}) underwent solid-state polymerizations upon ^{60}Co γ-irradiation. Anhydrous sodium propynoate $Na(O_2CC\equiv CH)$ was found to be the most reactive (up to 75% yield).[26] An X-ray crystal structure analysis revealed that the sodium ion and propynoate ligands formed a bilayer structure in which the sodium ion was five coordinate. The high reactivity was attributed to a very short distance (*e.g.* 3.29 Å) between aligned acetylenic reactive centers (Fig. 2).

Moloney and Foxman also demonstrated that dimethyl(propynoato)thallium formed the corresponding polypropynoate (conversion: 26%) upon exposure to either X-rays or ^{60}Co γ-ray irradiation.[27] Diaquabis(propynoato)magnesium exhibited less irradiation responsiveness and a lower conversion (22%), which was attributed to the lower absorption cross-section for both X-rays and ^{60}Co γ-rays. An X-ray crystal structure investigation revealed a 2D coordination polymer with four bridging carboxylates and a separation of 3.70 Å between acetylenic centers.[28] The acetylenic centers were nearly parallel. From this work, Foxman and co-workers concluded that the geometry criteria of the topochemical postulate were applicable to acetylenic systems.

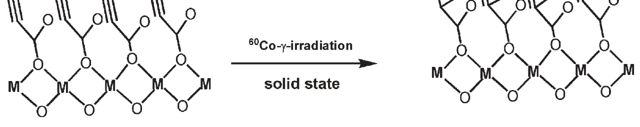


Fig. 2 Schematic representing the ^{60}Co γ-irradiation of $Na(O_2CC\equiv CH)$.

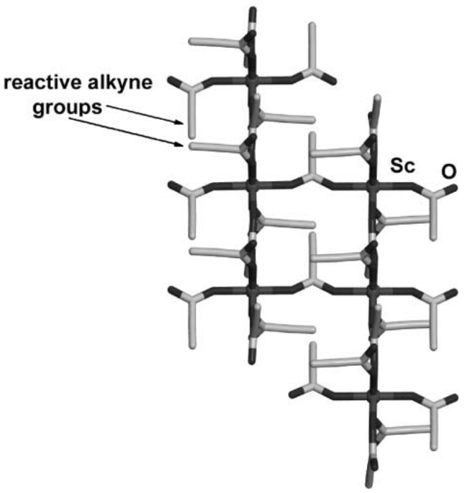


Fig. 3 View of the crystal structure of tris(propynoato)scandium(III) representing the orthogonal alignment of acetylenic moieties. Hydrogen atoms omitted for clarity.

Although the topochemical postulate served as a guide for the polymerization of alkynoates, the polymerization of tris(propynoato)scandium(III) was an exception (Fig. 3).[29] The solid was shown by Foxman and co-workers to contain infinite chains with short $-C\equiv C\cdots C\equiv C-$ contacts between adjacent acetylene moieties. The chains however, were aligned in a nearly orthogonal fashion. Despite the orthogonal orientation, the carboxylates polymerized upon exposure to ^{60}Co γ-irradiation to form the corresponding polypropynoate in up to 55% yield.

Whereas the majority of solid-state polymerizations had been shown to occur within coordination polymers, Foxman and co-workers also described a solid-state polymerization that occurred between discrete binuclear metal complexes. In particular, dinuclear $La_2(O_2CC\equiv CH)_6(H_2O)_4\cdot 2H_2O$ was shown to give the corresponding polypropynoate in up to 59% yield upon ^{60}Co γ-irradiation (Fig. 4).[30] An X-ray crystal

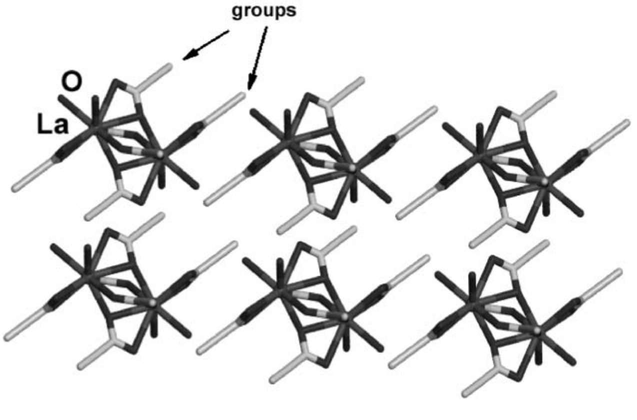


Fig. 4 Crystal structure of diaquabis(propynoato)lanthanum. Hydrogen atoms omitted for clarity.

structure investigation of the solid revealed lanthanum dimers, in which the metal atoms were nine-coordinate and separated by a distance of 4.14 Å. O–H···O and C–H···O hydrogen bonds linked the dimers to give hydrogen-bonded sheets in the crystallographic *bc* plane. The acetylenic centers were aligned parallel and separated by a distance of 3.95 Å. An analogous 2,2-bipyridine-based solid was shown to be unreactive.

In addition to monocarboxylates, dicarboxylates have been used to support metal-mediated polymerizations in the solid state.[31] In particular, Michaelides and co-workers have recently demonstrated the formation of 2D and 3D coordination polymers that involve the complexation of acetylenedicarboxylate dianion (ADC^{2-}) with heavy metals such as La^{2+}, Ce^{3+} and Cd^{2+}. The polymers possessed chains with short contacts between neighboring carbon–carbon triple bonds. Upon heating, the crystalline solids reacted to form the corresponding polycarboxylates.

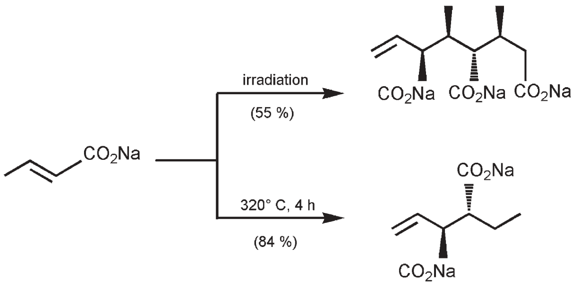
2.2 Oligomerizations

As stated, metal ions can be used to mediate the formation of oligomers in the solid state (Table 2). In contrast to polymers, which consist of an infinite number of monomers, oligomers contain a smaller and finite number of such units.

To our knowledge, Naruchi *et al.* reported the first example of a metal-mediated solid-state reaction that involved the exclusive formation of oligomers. In particular, upon heating below 190 °C, Ca^{2+} methacrylates formed two dimers: α-methylene-γ,γ-dimethylglutarate (MDMG) and α-methylene-δ-methyladipate (MMDP).[32] Above 170 °C a trimer, 1-nonene-2, 5,8-tricarboxylate (NTC) formed. Similarly, Ba^{2+} methacrylates formed both MDMG and MMDP above 170 °C and two trimers NTC and 4-methyl-1-octene-2,4,7-tricarboxylate (MOTC) above 190 °C. Sr^{2+} and Mg^{2+} methacrylates gave only MDMG and NTC. A mixture of tetramers was also observed when the solids were exposed to a higher temperature (*e.g.* 300–350 °C).

In subsequent work, Foxman and co-workers showed that a number of alkenoates could be used to generate oligomers. In particular, ^{60}Co γ-irradiation of $Na(O_2CCH{=}CHCH_3)$ (Scheme 4) formed a mixture of oligomers, which remarkably contained 75–80% of one the eight possible diastereoisomers of the trisodium salt of 2,4-dimethyl-6-heptene-1,3,5-tricarboxylic acid in 70–80% conversion.[33]

The corresponding triacid was obtained by neutralization with hydrochloric acid in up to 55% yield (Fig. 5). A lack of single-crystal X-ray data prevented a detailed explanation behind the unprecedented stereoselectivity of the reaction. A unit cell determination, however, revealed an unusually short *c*-axis, which was highly suggestive of –C=C···C=C– distances of <3.47 Å. It was also suggested that the formation of the head-to-tail trimer was based on an anionic chain reaction. In contrast, heating of the material afforded a disodium salt of 3-methyl-4-pentene-1,2-dicarboxylic acid, which was consistent with a head-to-head arrangement of the anions in the solid.[34]



Scheme 4

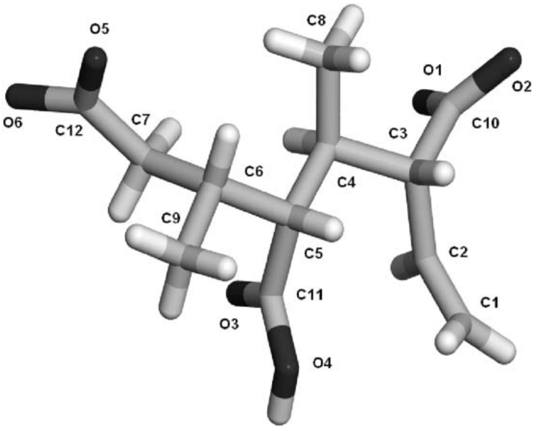


Fig. 5 Crystal structure of 2,4-dimethyl-6-heptene-1,3,5-tricarboxylic acid (two carboxylic acid hydrogen atoms not included in the structure).

Foxman and co-workers have also reported the unexpected and high-yield formation of a stereoregular oligomer based on the trimerization of terminal vinyl groups in anhydrous bis(but-3-enoato)zinc.[35] The structure of the complex contained zinc but-3-enoates packed in a bilayer motif with distance of 4.42 Å between alkene moieties (Fig. 6). ^{60}Co γ-irradiation of the solid resulted in the formation of isotactic zinc oligomer of but-3-enoate in 49% yield.

Crystalline metal pentenoates (*e.g.* Li, Na, K, Mg, Ca, Sr, Ba, Zn, Cd, Pb) have also been shown by Di and Foxman to

Table 2 Solid-state oligomerizations mediated by metal ions

Compound	Method	Yield (%)	Ref.
CaMA	Thermal annealing (160–350 °C)	10;[a] 58;[a] 12[a]	32
BaMA	Thermal annealing (160–350 °C)	22;[a] 41;[a] 21;[a] 24[a]	32
MgMA	Thermal annealing (160–350 °C)	16;[a] 6[a]	32
SrMA	Thermal annealing (160–350 °C)	34;[a] 22[a]	32
$Na(O_2CCH{=}CHCH_3)$	^{60}Co γ-ray irradiation (72 Mrad)	55	33
$Zn_2(O_2CCH{=}CHCH_3)_2$	^{60}Co γ-ray irradiation (1570 Mrad)	49	35
Metal pentenoates (*e.g.* Na, Cs, Sr, Ba)	^{60}Co γ-ray irradiation (72 Mrad)	17–84	36

[a] Yields correspond to the maximum yields reported for oligomers MDMG, MMDP, NTC and MOTC.

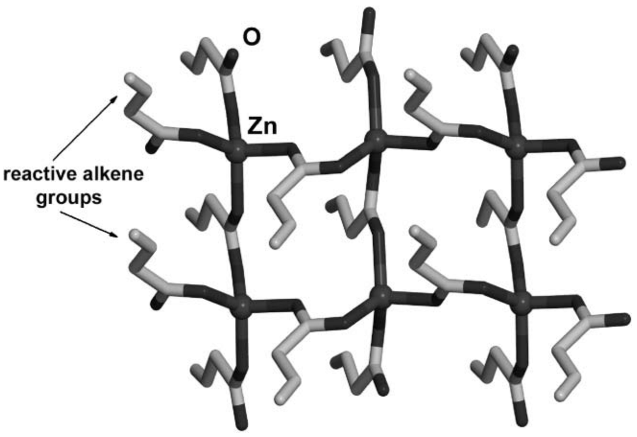


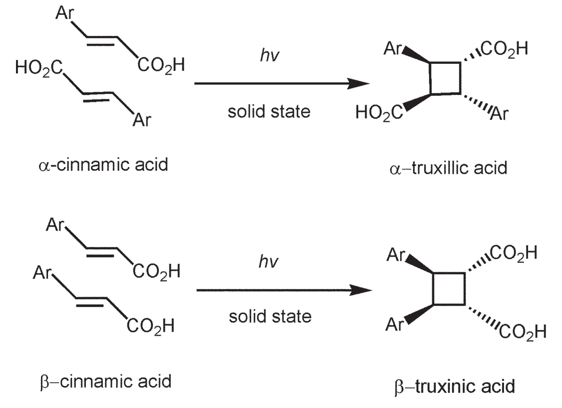
Fig. 6 View of the crystal structure of bis(but-3-enoato)zinc. Hydrogen atoms are omitted for clarity.

lead to acetylacrylates (17–84% conversion) and insoluble oligomers upon ^{60}Co γ-irradiation irradiation in air.[36] In contrast, ^{60}Co γ-irradiation *in vacuo* resulted in the formation of complex mixtures of both oligomers and dimers.

2.3 Dimerizations

In general, two types of dimerizations have been observed using metals in the solid state; namely, the [2 + 2] photodimerizations and radical dimerizations (Table 3).

The majority of metal-mediated dimerizations have involved photodimerizations. As stated, Cohen and Schmidt determined the geometry criteria for a [2 + 2] photodimerization in the solid state.[9] The criteria, being part of the topochemical postulate, were derived from studies involving α-, β-, γ-polymorphs of cinnamic acid (Scheme 5). Although the earliest examples of metal-mediated [2 + 2] photodimerizations in the solid state were achieved largely by discovery, the most recent examples have been achieved by design where principles of supramolecular chemistry and coordination-driven self-assembly have been used to preorganize olefins for reaction.



Scheme 5

Studied to a lesser extent have been radical dimerizations, which can be induced by either heat or γ-rays. Work in this area has been performed by Naruchi *et al.* on the thermal dimerization of alkali-metal salts of crotonic acid and Foxman and co-workers on γ-ray-induced dimerizations of metal alkenoates. Each metal system has involved either a mononuclear complex, binuclear complex, or coordination polymer that assembles the reactive sites for reaction.

2.3.1 Mononuclear metal complexes. To our knowledge, Praetorius and Korn reported the first example of a [2 + 2] photodimerization mediated by a metal ion in the solid state.[37] Upon UV-irradiation, the mononuclear complex of uranyl chloride and *trans*,*trans*-dibenzylideneacetone (dba) resulted in a stereospecific formation of the "truxillic" type dimer *rctt*-1,3-bis(3-phenylprop-2-enol-oxo)-2,4-bis(phenyl)cyclobutane. Stobbe and Färber later reported the formation of the same dimer using $SnCl_4$.[38] To reveal the role of the uranyl ion on the solid-state reactivity, Alcock *et al.* determined the X-ray crystal structures of both unsolvated and solvated forms of the uranyl chloride–dba complex: $[(UO_2)Cl_2(dba)_2]$ and $[(UO_2)Cl_2(dba)_2]\cdot 2CH_3CO_2H$.[39] The uranium ions adopted an octahedral conformation surrounded by two chlorine atoms,

Table 3 Solid-state dimerizations mediated by metal ions

Compound	Method	Yield (%)	Ref.
2 : 1 Complex methyl cinnamate–$SnCl_4$	UV irradiation	70	41
2 : 1 Complex ethyl cinnamate–$SnCl_4$	UV irradiation	85	41
2 : 1 Complex *n*-propyl cinnamate–$SnCl_4$	UV irradiation	45	41
2 : 1 Complex isopropyl cinnamate–$SnCl_4$	UV irradiation	6	41
2 : 1 Methyl *p*-(trifluoromethyl)cinnamate–$SnCl_4$	UV irradiation	22	41
2 : 1 Methyl *p*-chlorocinnamate–$SnCl_4$	UV irradiation	25	41
2 : 1 Methyl methyl-*p*-cinnamate–$SnCl_4$	UV irradiation	85	41
2 : 1 Methyl α-methylcinnamate–$SnCl_4$	UV irradiation	23	41
2 : 1 Methyl indenoate–$SnCl_4$	UV irradiation	61	41
$[Zn_4L_2(OH)_2(4,4'\text{-bpe})_2](ClO_4)_4\cdot 4H_2O$	UV irradiation	100	8*b*
$[Ag_2(4\text{-stilbz})_4][CO_2CF_3]_2$	UV irradiation	100	42
$Ca_2(O_2CCH{=}CHCH_3)_2$	^{60}Co γ-ray irradiation (1.4 Mrad)	76	43
$Na(O_2CCH{=}CHCH_3)$	Thermal annealing (250–320 °C)	90[a]	44
$K(O_2CCH{=}CHCH_3)$	Thermal annealing (250–320 °C)	28[a], 27[a], 5[a]	44
$[Cd_2(O_2CCH{=}CHCO_2]\cdot 2H_2O$	UV irradiation	100	46
$[\{CF_3CO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-bpe})_2]_n$	UV irradiation	100	47
$[Zn_4L(OH)(4,4'\text{-bpe})_2](ClO_4)_4\cdot 4H_2O$	UV irradiation	95	48
$[Ag(\mu\text{-bpe})(H_2O)](CF_3CO_2)\cdot CH_3CN$	UV irradiation	100	49

[a] Yields correspond to maximum yields reported for oligomers HEDC, MPEDC and DMBEDC.

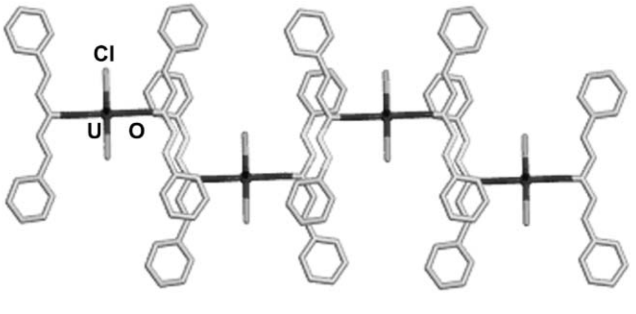


Fig. 7 Crystal structure of dba and uranyl chloride complex. Reactive alkene groups highlighted. Hydrogen atoms are omitted for clarity.

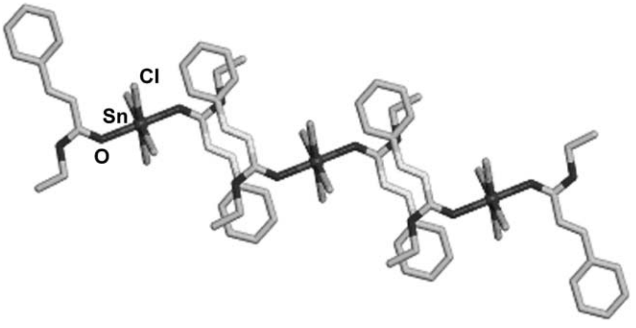


Fig. 8 Crystal structure of 2 : 1 ethyl cinnamate-$SnCl_4$ complex illustrating the parallel alignment of cinnamate ligands. Hydrogen atoms are omitted for clarity. The reactive alkene groups highlighted.

two oxygen atoms of the uranyl group, and two keto-oxygen atoms of the dba ligand (Fig. 7). The dba moieties in both structures exhibited a *trans*,*trans*-conformation and planar orientation. Distances between the alkenes of adjacent dba moieties were 4.09 and 3.51 Å for the unsolvated and solvated forms, respectively. In a later and related study, Theocharis revealed that solids formed on complexation of Ni^{2+}, Cu^{2+}, Zn^{2+} and series of substituted cyclopentanones underwent cross-linking [2 + 2] photodimerizations.[40]

Lewis *et al.* have demonstrated that [2 + 2] photoreactivity of a series of cinnamic esters can be mediated by Lewis acids (*e.g.* $SnCl_4$).[41] The cinnamic esters formed 1 : 1 complexes with BF_3 and 2 : 1 complexes with $SnCl_4$, which upon UV-radiation ($\lambda > 300$ nm) led exclusively to the formation of ''truxillic'' type dimers (Table 3). X-Ray crystal analysis of the 2 : 1 ethyl cinnamate–$SnCl_4$ complex revealed an octahedral conformation adopted by the Sn^{4+} ion (Fig. 8). The reaction occurred between neighboring cinnamate ligands. The ligands were planar, stacked in a head-to-tail fashion, and separated by 4.12 Å.

2.3.2 Binuclear metal complexes. Our group has reported the first intermolecular [2 + 2] photodimerization based on a binuclear metal complex.[8a] In particular, Schiff-base Zn^{2+} complexes of general composition $[Zn_4L_2(OH)_2(4,4'\text{-bpe})_2](ClO_4)_4\cdot 4H_2O$ (where LH = 2,6-bis[*N*-(2-pyridylethyl)formimidoyl]-4-methylphenol; 4,4′-bpe = *trans*-1,2-bis(4-pyridyl)ethylene) were used to assemble two molecules of 4,4′-bpe in a position suitable for [2 + 2] photodimerization (Fig. 9). An X-ray diffraction analysis revealed the formation of the tetranuclear assembly held together by four Zn–N bonds. The olefins were aligned parallel and at distance of 3.64 Å. UV-irradiation of the complex using either 419 nm light or a broadband Hg lamp led to the quantitative and stereocontrolled formation of *rctt*-tetrakis(4-pyridyl)cyclobutane (4,4′-tpcb). The [2 + 2] photodimerization was shown to occur *via* a single-crystal-to-single-crystal transformation (SCSC). To the best of our knowledge, this study represented the first example of a metal-mediated SCSC [2 + 2] photodimerization. The solid also exhibited different fluorescent emissions (*i.e.* blue to green) before and after the photoreaction.

The binuclear approach has also been expanded to an Ag^+ solid. In particular, $[Ag_2(4\text{-stilbz})_4][CO_2CF_3]_2$ (where 4-stilbz = *trans*-1(4-pyridyl)-2-(phenyl)ethylene) was shown to undergo a [2 + 2] photodimerization upon UV-irradiation with either 419 nm light or a broadband Hg lamp. The photodimerization occurred regiospecifically and in quantitative yield *via* a SCSC transformation (Fig. 10).[42] An X-ray crystal structure analysis revealed a dinuclear complex held together by argentophilic forces (Ag···Ag distance of 3.41 Å). The olefinic centers were antiparallel and separated by 3.82 Å. The photodimerization led to significant long-range movement of the Ag^+ ions, as well as rotations of the olefins and carboxylate groups. Consequently, the reaction of the binuclear complex transformed the finite complex into a 1D coordination network.

2.3.3 Coordination polymers. The design and construction of coordination polymers with organic units that dimerize in the solid state is attracting much interest.[8b] By having the metal and organic units linked infinitely in up to three dimensions, coordination polymers have provided a means to control the properties of molecular solids. Metal–organic frameworks are considered promising for applications in various areas of

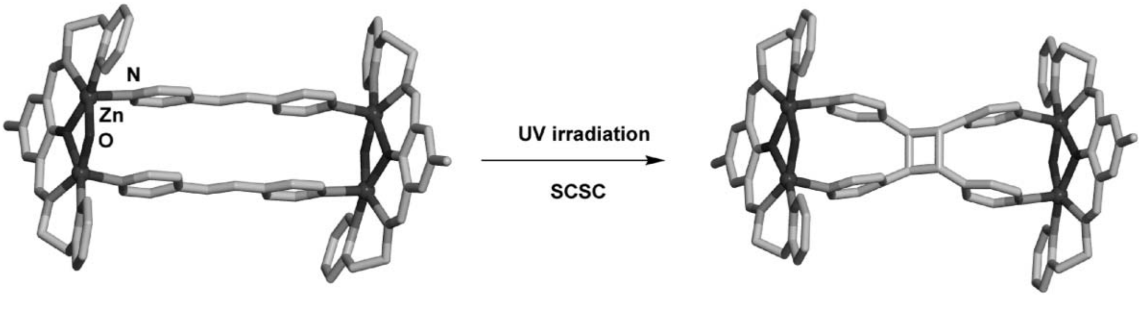


Fig. 9 Crystal structures of $[Zn_4L_2(OH)_2(4,4'\text{-bpe})_2](ClO_4)_4\cdot 4H_2O$ before and after the photoreaction.

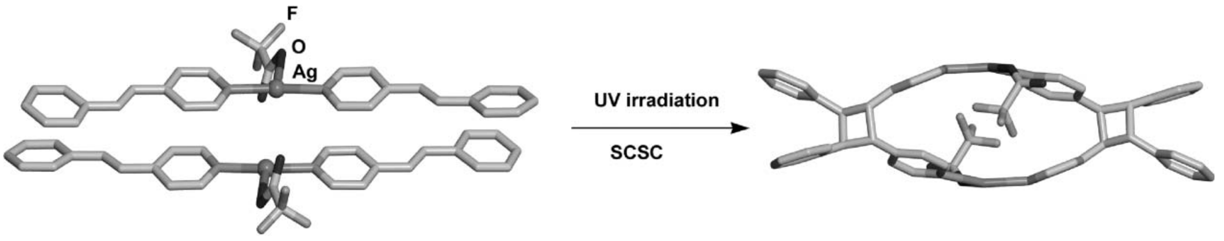


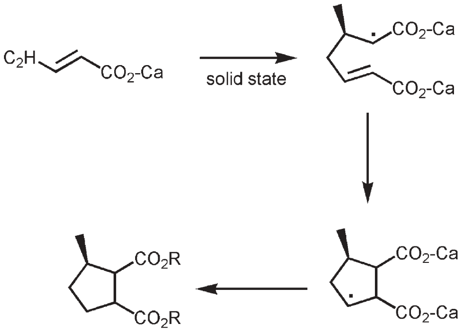
Fig. 10 Crystal structure of $[Ag_2(4\text{-stilbz})_4][CO_2CF_3]_2$ before and after photoreaction.

materials science (*e.g.* optical, magnetic). Moreover, it is reasonable to expect that the integration of reactive groups that dimerize can provide an additional means to modify and control the properties of these solids.

To our knowledge, Foxman and co-workers were the first to unequivocally demonstrate the formation of an organic dimer from a coordination polymer. In particular, the group showed that ^{60}Co γ-ray irradiation can induce a solid-state radical dimerization in bis(*trans*-but-2-enoato)calcium.[43] The reaction led to the stereospecific formation of only one of the four possible diastereomers (*e.g. cis*,*trans*-nepetic acid) in 76% yield at 10% conversion (Scheme 6).

An X-ray crystal structure analysis showed that the solid was based on a 2D coordination polymer in which each Ca^{2+} ion adopted an octahedral coordination environment (Fig. 11). The stereochemistry of the product suggested an intermolecular reaction involving an addition of an allyl radical of one butenoate moiety to the β-carbon of another.

Earlier work of Naruchi and Miura has also described radical dimerizations in coordination polymers. It was shown that sodium and potassium crotonates dimerized upon heating in the temperature range of 295–320 °C.[44,45] The thermal reaction of Na^+ crotonate led exclusively to the formation of hex-1-ene-3,4-dicarboxylate (HEDC) in nearly quantitative yield. In contrast, K^+ crotonate formed three isomeric dimers: HEDC, 4-methylpent-2-ene-3,5-dicarboxylate (MPEDC) and 2,3-dimethylbytent-1-ene-1,4-dicarboxylate (DMBEDC) under the same conditions. The structure of the starting materials, however, has not yet been determined using single-crystal X-ray diffraction.



Scheme 6

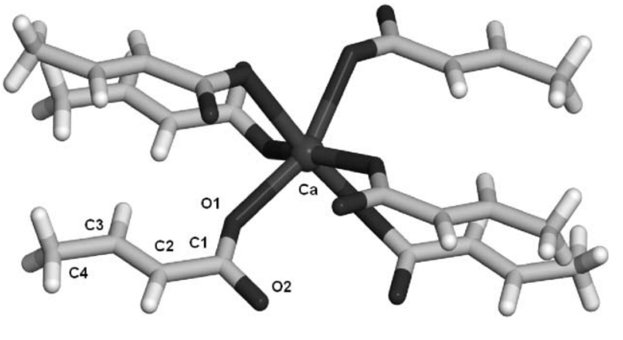


Fig. 11 Crystal structure of bis(*trans*-but-2-enoato)calcium.

Recently, Michaelides *et al.* have described the first photoreactive metal-coordination network $[Cd_2(O_2CCH{=}CHCO_2]\cdot 2H_2O$.[46] The components of the solid formed a 2D grid. Fumarate units of the nearest-neighbor grids underwent a stereocontrolled [2 + 2] cycloaddition reaction that formed of *trans*,*trans*,*trans*-1,2,3,4-cyclobutanetetracarboxylic acid in quantitative yield. An X-ray diffraction analysis revealed short contacts of 3.34 Å between the alkenes (Fig. 12).

Shortly following the work of Michaelides, Vital and co-workers reported the photoreactive coordination polymer $[\{CF_3CO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-bpe})_2]_n$.[47] An X-ray diffraction analysis revealed the formation of a 1D ladder-like polymer in which pairs of Zn^{2+} ions (Zn···Zn distance: 3.89 Å) adopted distorted octahedral geometries. The Zn^{2+} ions were bridged by two acetato ligands, a trifluoroacetate anion, and four molecules of 4,4′-bpe (Fig. 13). The alkenes were aligned parallel and separated by a distance of 3.75 Å. UV-irradiation of the solid led to the stereocontrolled formation of 4,4′-tpcb. The reaction occurred *via* a SCSC transformation.

In related work, our group has demonstrated the formation of the 1D ladder-like photoreactive coordination polymer $[Zn_2L(OH)(4,4'\text{-bpe})_2](ClO_4)_2\cdot 4H_2O$ (Fig. 14).[48] An X-ray diffraction analysis revealed that the 4,4′-bpe molecules were oriented parallel and separated by 3.71 Å. The formation of 4,4′-tpcb occurred in up to 95% yield upon UV-irradiation (broadband medium pressure Hg-lamp) over a period of 32 h.

Whereas argentophilic forces have been used to direct reactivity within a binuclear complex, Nagarathinam and Vital

Fig. 12 Representation of three adjacent layers of the coordination network $[Cd_2(O_2CCH{=}CHCO_2]\cdot 2H_2O$.

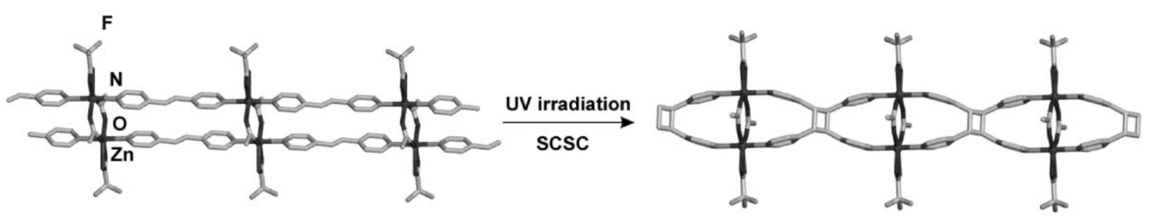


Fig. 13 Representation of SCSC [2 + 2] cycloaddition reaction of $[\{CF_3CO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-bpe})_2]_n$.

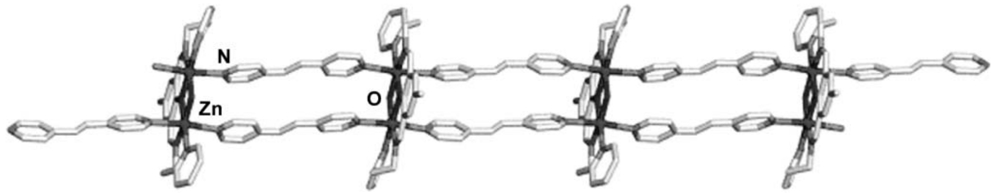


Fig. 14 Crystal structure of $[Zn_2L(OH)(4,4'\text{-bpe})_2]^{2+}$.

have recently reported a [2 + 2] photodimerization within the desolvated 1D coordination polymer $[Ag(\mu\text{-bpe})(H_2O)](CF_3CO_2)\cdot CH_3CN$.[49] The olefins of the solvated structure were misaligned and separated at a distance of 5.17 Å. Desolvation of the polymer, however, resulted in an unusual solid-state reorganization that lead to the formation of a ladder-like polymer. Cooperative anisotropic molecular movement of the components upon desolvation was proposed and supported by X-ray powder diffraction analyses.[50]

3 Concluding remarks and future scope

This review has focused on the use of metal ions to mediate chemical reactivity in the organic solid state. Whereas early work in this field focused upon the solids that exhibit reactivity, recent developments in the field of supramolecular chemistry have enabled chemists to preorganize reactive sites using directional forces so as to achieve reactivity by design. Consequently, the construction of solids that employ metals to direct reactivity of organics in the solid state has gained a new perspective with a possibility of designing solids in which chemical reactivity is combined with additional bulk physical properties (*e.g.* magnetic). While considerable progress has been made, it is clear that the field of metal-mediated reactions of organic molecular species in the solid state remains at a stage where many additional studies to engineer new reactive materials has yet to be accomplished.

Acknowledgements

We thank the National Science Foundation (CAREER Award, L.R.M., DMR-0133138) for financial support.

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