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Photochemically reactive polymers; the synthesis and photochemistry of amide polymers and model compounds containing metal–metal bonds and internal radical traps

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Abstract

The synthesis and photochemistry of a photochemically reactive polymer that has internal metal-radical traps (chlorine atoms) along its backbone is reported. Reaction of the organometallic 'diamine' $(CpCH_2CH_2NH_2)_2Mo_2(CO)_6$ with an activated mixed anhydride derivative of 3,4-dichlorohexanedioic acid gave the polymer $[-CHClCH_2C(O)NHCH_2CH_2(\eta^5\text{-}C_5H_4)(CO)_3Mo-Mo(CO)_3(\eta^5\text{-}C_5H_4)CH_2CH_2NHCOCH_2CHCl-]_n$. The difunctional activated mixed anhydride was used because the Mo–Mo bond reacts with acyl chlorides to form oligomeric amides containing $-Mo(CO)_3Cl$ units. As an aid to the spectroscopic characterization of the polymers, model complexes were synthesized by reacting $(CpCH_2CH_2NH_2)_2Mo_2(CO)_6$ with activated mixed anhydrides of chloroacetic acid and 5-chlorovaleric acid. Thus, $(\eta^5\text{-}C_5H_4R)_2Mo_2(CO)_6$ ($R = -CH_2CH_2NHCOCH_2Cl$ and $-CH_2CH_2NHCO(CH_2)_3CH_2Cl$) were synthesized by reacting $(CpCH_2CH_2NH_2)_2Mo_2(CO)_6$ with $CH_3CH_2OC(O)OC(O)CH_2Cl$ and $CH_3CH_2OC(O)OC(O)(CH_2)_3CH_2Cl$, respectively. Because of the metal–metal bonds along the backbone, the polyamide is photochemically reactive (as are the model complexes), undergoing metal–metal bond photolysis reactions similar to the $Cp_2Mo_2(CO)_6$ dimer. The products contain $CpMo(CO)_3Cl$ units, indicative of 'self-trapping' by the chlorine atoms built into the polymer and model complexes. Photochemical decomposition also occurred in the solid state without external metal-radical traps. © 1998 Elsevier Science S.A.

Keywords: Amide polymers; Metal–metal bonds; Photochemical decomposition

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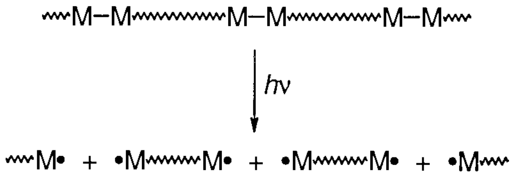
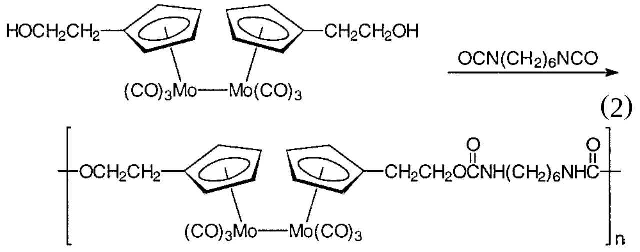
1. Introduction

Photochemically reactive polymers [1–4] are of considerable interest because they are useful as degradable plastics [5], photoresists [6–10], biomedical materials, and as precursors to ceramic materials [6–8,11–14]. In previous papers, we described the synthesis of a new class of photodegradable polymers that have metal–metal bonds along the polymer backbone [15–18]. These polymers are photochemically active because metal–metal bonds can be cleaved with visible light [19,20].



(1)

Our syntheses of metal–metal bond-containing polymers use metal–metal bonded dimers with functionally substituted cyclopentadienyl ligands, a synthetic methodology borrowed from earlier work on polyferrocenes [21–30]. An example of a polyurethane synthesis is shown in Eq. (2) [15].



(2)

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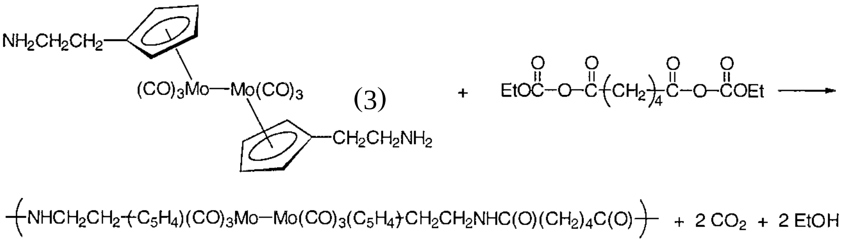
Thus far, polyurethanes, polyureas, polyethers, polyvinyls, polyamides and several types of copolymers with metal–metal bonds along the backbone have been synthesized [15–18]. As predicted, all of these polymers are photodegradable, both in solution and in the solid state, provided that a metal radical trap is present to capture the metal radicals and prevent reformation of the metal–metal bond by radical recombination [15–18]. In solution, CCl_4 or other organic halides are excellent traps, while ambient oxygen serves that purpose in the solid state reactions.

Our long-range goal is to develop ways to control the rate of photodegradation of these polymers. Two methods are being investigated. One approach is to vary the number of metal–metal bonds along the polymer backbone, and the other is to control the efficiency with which the photogenerated metal radicals are captured. (The capture efficiency will affect the rate of degradation because the metal radicals can back-react to reform the metal–metal bond). To control (and enhance) the rate of radical trapping, we are designing polymers with radical traps built into the backbone. It is our hypothesis that it should be possible to control more easily the degradation of polymers with built-in radical traps because the concentration of the trap can be manipulated. This paper reports on our synthesis of a polymer and several model complexes that have radical traps (chlorine atoms) attached to the polymer backbone. The photochemistry of these species is also reported.

2. Results and discussion

2.1. Synthetic strategy

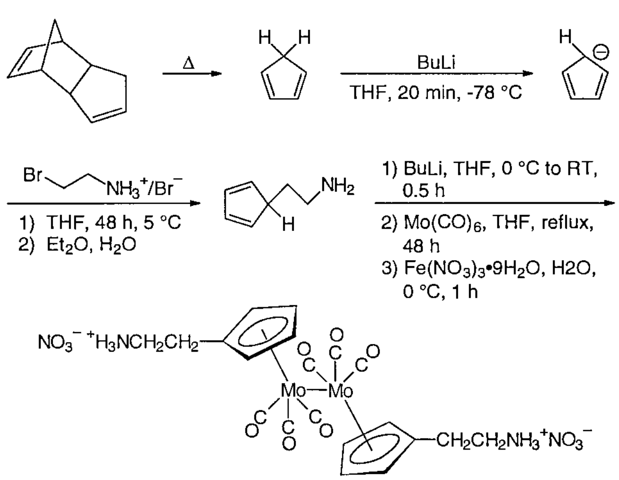
Selected organic halides are excellent traps for metal radicals. It was decided therefore to substitute the polymer backbones with halogens to test the feasibility of synthesizing a polymer with a built-in radical trap. These polymers would then be used to test the hypothesis that a built-in radical trap can enhance the rate of photodegradation. Although these premises could be investigated with numerous types of polymers, our recent studies of photodegradable polymers have focused on polyamides [18]; therefore, polyamides were also used in this study. Polyamides with metal–metal bonds along the backbone are synthesized by the reaction of $(CpCH_2CH_2NH_2)_2Mo_2(CO)_6$ with activated mixed anhydride derivatives of carboxylic acids (e.g., Eq. (3)). (As in our previous study of polyamides with metal–metal bonds [18], $(CpCH_2CH_2NH_2)_2Mo_2(CO)_6$ was generated in situ by deprotonation of $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$ using triethylamine. The dimer is prepared and stored as the ammonium salt to prevent reaction of the free amine with the metal–metal bond [31].) For this study, the plan was to incorporate halogens along the backbone by using halogen-containing activated mixed anhydride derivatives of carboxylic acids.



(3)

2.2. A new synthesis of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$

Our previously reported synthesis of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ was long and tedious [18]. It involved five steps and required nearly 10 days of intensive labor in order to obtain analytically pure material. To expedite this investigation, and improved synthesis was developed that has fewer steps, requires much less time (about 6 days), and gave the dimer in higher yield (Scheme 1). [1]



Scheme 1. Improved synthesis of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$.

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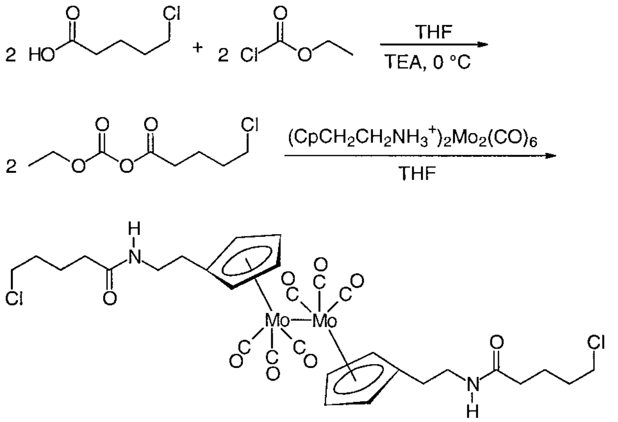
[1] This new preparation of the amine ligand is a modification of the one mentioned in a *personal communication* from Camil Joubran and Professor Douglas Grotjahn, Department of Chemistry, Arizona State University, Tempe, AZ, USA 85287-1604.

The new synthesis utilized the reaction of two equivalents of cyclopentadienyl anion (generated in situ with *n*-butyl lithium in THF) with 1 mol of 2-bromoethylamine hydrobromide in THF. After drying, the amine ligand was isolated as a pure, clear, yellow oil in 78% yield. This new route resulted in the isolation of the amine ligand in fewer steps and without need for purification. (A difficult distillation was required in the original synthesis.) The $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ dimer was then synthesized using $Mo(CO)_6$ as previously described (26% yield) [17]. As previously noted, the dimer is air sensitive in solution, but relatively stable in the solid state if it is kept in the dark. Spectroscopic data are reported in Table 1.

2.3. Synthesis of model compounds

To facilitate the synthesis and characterization of the new polymers, model compounds were synthesized first using halogen-containing activated mixed anhydride derivatives of *mono*carboxylic acids. These syntheses and other exploratory experiments revealed that bromine-containing carboxylic acids were not satisfactory because the resulting products were too reactive. For example, in the reaction with α-bromovaleric acid ($CH_3(CH_2)_2CH_2BrCOOH$), the product was an elastomeric solid, vaguely characterized to be an α-amino cross-linked bis-amide network polymer formed by nucleophilic attack of the amine on the α carbon. Other experiments showed that, with the exception of chloroacetic acid, chlorine atoms could not be in the α-position relative to the amide linkage; the resulting products were again too reactive to isolate and characterize. For these reasons, 5-chlorovaleric acid, $CH_2Cl(CH_2)_3COOH$, was used in this study.

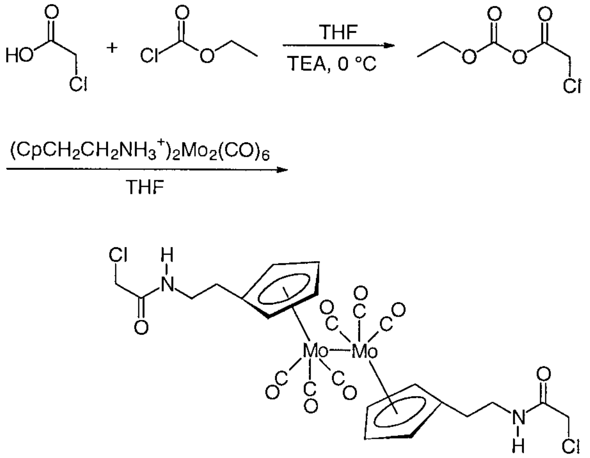
Previous work showed that carboxylic acids do not react readily with $(CpCH_2CH_2NH_2)_2Mo_2(CO)_6$ and that acid chlorides react to cleave the metal–metal bonds and form $CpMo(CO)_3Cl$-containing species [18]. However, activated mixed anhydride derivatives of the acids were reactive and gave good yields of the amide products without degrading the metal–metal bonds. Similar results were obtained using 5-chlorovaleric acid. Thus, the direct reaction with $(CpCH_2CH_2NH_2)_2Mo_2(CO)_6$ gave no amide product. However, the activated mixed anhydride of 5-chlorovaleric acid in THF gave model complex, **1**, as shown in Scheme 2. The product was isolated by precipitation from THF/hexanes as an air stable (in the absence of light) red powder. (This color is similar to the many other model compounds and polymers containing Mo–Mo bonds [15–18].) The presence of the amide linkage was indicated by an amide resonance in the ^1H NMR at 7.04 ppm, and the $Cp_2Mo_2(CO)_6$ structural unit was indicated by $\nu(C\equiv O)$ at 2006, 1950, and 1906 cm^{-1}. (For comparison, $Cp_2Mo_2(CO)_6$ has bands at 2006, 1950, and 1906 cm^{-1} in THF [15].) Amide bands were seen at 3431, 2919, 2850, 1644, 1469, and 1244 cm^{-1}, and the electronic absorption spectrum had peaks at 508 and 393 nm (Table 1), assigned to the $d\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions of the Mo–Mo chromophore, respectively [19,20].



1

Scheme 2. Synthesis of model compound **1** from 5-chlorovaleric acid and $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$.

Another model complex, **2**, was synthesized by a similar procedure using chloroacetic acid (Scheme 3). Again, the product was isolated by precipitation from THF/hexanes as an air stable (in the dark) red powder. An amide resonance was observed in the ^1H NMR at 7.08 ppm and $\nu(C\equiv O)$ bands were observed at 2013, 1950, and 1906 cm^{-1}. Amide stretches were observed at 3444, 3081, 2850, 1644, 1469, and 1256 cm^{-1}. The electronic spectrum has peaks at 509 and 392 nm, which confirm the presence of Mo–Mo bonds. Elemental analysis also confirmed the proposed empirical formula.



2

Scheme 3. Synthesis of model compound **2** from chloroacetic acid and $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$.

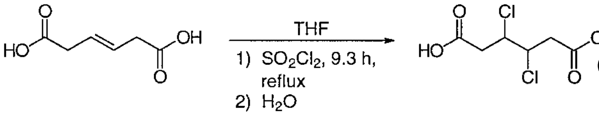
Table 1
Selected spectroscopic data

Compound	^{1}H NMR[a] δ (in ppm)	IR[b] υ (in cm^{-1})	UV–Vis[c] λ (in nm)	Reference
$Cp_2Mo_2(CO)_6$	5.60 (br), 5.44 (br)[c]	2012 (sh, w), 1954 (s), 1925 (m), 2011 (m), 1959 (s), 1913 (s)[d]	508, 388	[18]
$CpMo(CO)_3Cl$	5.70[e]	2051 (s), 1972 (vs)[b]		[16]
$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6]–[NO_3]_2$	5.49–5.38 (m,8H), 3.14 (t,2H), 2.78 (t, 2H)[f]	2009 (m), 1958 (s), 1908(s)[g]	503,388[g]	[31]
1	7.04 (s, br, 2H), 5.39 (s, br, 4H), 5.20 (s, br, 4H), 3.28 (m, 4H), 2.56 (t, 4H), 2.05 (t, 4H), 1.58 (m, 4H), 1.29 (s, br, 64H), 0.89 (t, 6H)[h]	3431 (m), 2919 (vs), 2850 (s), 2006 (s), 1950 (vs), 1906 (vs), 1644 (m), 1469 (w), 1244 (w) 1644 (m), 1469 (w), 1244 (w)	508, 393	[18]
2	7.08 (s, br, 2H), 5.39 (s, br, 4H), 5.20 (s, br, 4H), 3.28 (m, 4H), 2.56 (t, 4H), 2.06 (t, 4H), 1.58 (m, 4H), 1.29 (s, br, 44H), 0.89 (t, 6H)[h]	3444 (m), 3081 (w), 2850 (m), 2013 (m), 1950 (vs), 1906 (vs), 1644 (m), 1469 (w), 1256 (w)	509,392	This work
3	7.00 (s, br, 2H), 5.400 (s, br, 4H), 5.206 (s, br 4H), 4.034, 4.010, 3.986, 3.963 (m, 2H), 3.236, 3.214, 3.193, 3.170 (m, 4H), 2.589, 2.565, 2.542 (t, 4H), 2.492, 2.452 (d, 4H)[h]	3107 (w), 2016 (m), 1955 (vs), 1900 (vs), 1641 (m), 1471 (m), 1266 (m), 823 (m)	505,392	This work

[a] KBr.
[b] THF.
[c] Acetone-d_6.
[d] Acetone.
[e] CD_2Cl_2.
[f] D_2O.
[g] H_2O, pH 7 buffer.
[h] THF–d_8.

2.4. Synthesis of a polymer with chlorine atoms along the backbone

As was the case with the model complexes, the reactions of $(CpCH_2CH_2NH_2)_2Mo_2(CO)_6$ with dicarboxylic acids (or their derivatives) that have chlorine atoms in the α position failed to yield stable products. For that reason, 3,4-dichlorohexanedioic acid was synthesized by chlorinating *trans*-β-hydromuconic acid. The synthesis was a modification of a literature procedure for chlorination of an alkene using thionyl chloride [32]. The synthesis is outlined in Eq. (4).

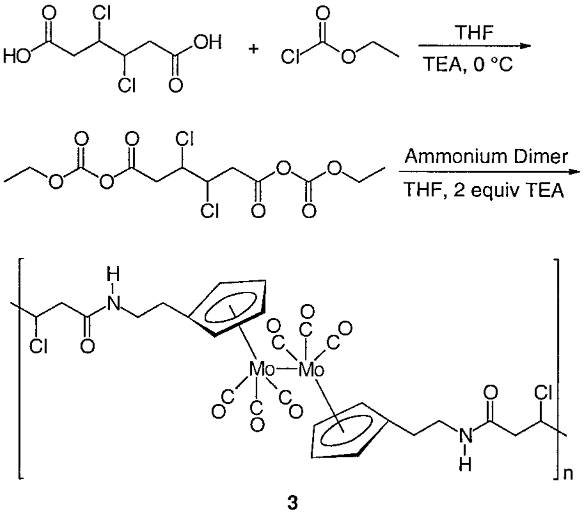


(4)

The chlorinated material was characterized by ^1H and ^{13}C NMR and by infrared spectroscopy (see Section 3). Complete incorporation of chlorine atoms was not achieved; ^{13}C NMR and elemental analysis indicated about 1.5 Cl atoms were incorporated per molecule. However, this was not a concern as even partial incorporation of chlorine should affect the rate of polymer degradation.

The 3,4-dichlorohexanedioic acid was used in the synthesis of a polyamide by converting it to the activated mixed anhydride of the dicarboxylic acid and then reacting it in situ with $(CpCH_2CH_2NH_2)_2Mo_2(CO)_6$, as shown in Scheme 4.

The polymer product was isolated as a THF-soluble, air- and light-sensitive, tacky, red solid, similar in appearance to other polymers containing Mo–Mo bonds [15–18]. The polymer was spectroscopically similar to the model compounds. There was an amide resonance at 7.00 ppm, $\nu(C\equiv O)$ bands at 2016, 1955, and 1900 cm^{-1}, amide infrared bands at 3107, 1641, 1471, 1266, and 823 cm^{-1}, and peaks at 505 and 392 nm in the electronic spectrum. Elemental analyses showed the incorporation of approximately 1.5 chlorine atoms per repeat unit of the polymer backbone. Attempts to determine the molecular weight of the polymer by gel permeation chromatography were unsuccessful because the polymer decomposed on the column. However, previous work with other metal–metal bond-containing polymers would suggest a molecular weight in the range of 10,000–20,000 [15–18].



3

Scheme 4. Synthesis of a polyamide (**3**) with Mo–Mo bonds in the backbone and chlorine atoms along the backbone.

2.5. Photochemistry in solution

The photochemistry ($\lambda > 540$ nm) of model complexes **1** and **2** and of polymer **3** in degassed THF solutions (*with no added radical trap*) is similar. Spectroscopic monitoring of the photoreactions showed the disappearance of the Mo–Mo chromophore bands at ≈ 390 and ≈ 505 nm and of the $\nu(C\equiv O)$ bands at ≈ 2010, 1950, and 1910 cm^{-1}. In each case, new infrared bands appeared at 2046 and 1963 cm^{-1}, indicative of the $CpMo(CO)_3Cl$ unit. (For comparison, $CpMo(CO)_3Cl$ has bands at 2046 and 1963 cm^{-1} [33].) These experiments demonstrated that we had indeed synthesized a 'self-trapping' polymer. The quantum yields for the reactions of the model complexes in THF are 0.06 for compound **1** ($[\mathbf{1}] = 4.7 \times 10^{-4}$ M) and 0.05 for compound **2** ($[\mathbf{2}] = 2.6 \times 10^{-4}$ M). The quantum yield for disappearance of the polymer (9.3×10^{-4} M) is 0.02.

2.6. Photochemistry of polyamide films in the solid state

In previous studies with polyurethanes, polyureas, polyvinyls and polyethers containing metal–metal bonds [15–18], it was established that both light and oxygen are required for degradation to occur in the solid state. Air (oxygen) is necessary for the degradation to occur because oxygen traps the metal radicals produced by irradiation. In the absence of oxygen, the metal–metal bonds recombine and no net photolysis takes place. To test the hypothesis that the chlorine atoms in **3** can act as built-in metal-radical traps in solid state photoreactions (and that oxygen is therefore not necessary), thin films of **3** were exposed to ambient light in the absence of oxygen. (The films were kept under nitrogen.) For each film and its dark reaction control, the absorbance of the $d\pi \rightarrow \sigma^*$ transition was monitored periodically over a period of 50 days. In fact, when exposed to light, the films kept under nitrogen did decompose over the course of about 5 days (as indicated by the decrease in the $d\pi \rightarrow \sigma^*$ transition). In addition, infrared spectroscopy showed the appearance of new bands at 2048 and 1965 cm^{-1}, indicative of the $CpMo(CO)_3Cl$ unit. Other changes included a noticeable transformation in the surface appearance from smooth to fissured. From this data, we conclude that the photochemical decomposition of polymer **3** does not require oxygen, as is required by all of the other metal–metal bond-containing polymers synthesized thus far. Control experiments showed that films stored in the dark in air or under nitrogen showed no loss of absorbance in their $d\pi \rightarrow \sigma^*$ bands over 50 days. It is noteworthy that the rate of polymer **3** photodegradation could be increased by exposing it to oxygen. Comparison of samples irradiated in air to those kept under nitrogen showed that the photodegradation was about twice as fast in air.[2] This may simply be a result of having a higher concentration of trap present in the samples exposed to air. It is also interesting to note that diffusion in the polymer must be sufficiently large to allow the metal radicals and chlorine substituents to react.

In conclusion, the chlorine atoms along the backbone of polymer **3** can act as internal radical traps for the metal radicals produced by photolysis of the metal–metal bonds. Future work in our laboratory is directed at controlling the rate of polymer degradation by studying how the concentration of internal trap affects the rate of degradation.

3. Experimental

All air-sensitive manipulations were carried out under nitrogen using standard Schlenk line techniques or a Vacuum Atmospheres glovebox.

3.1. Materials

Tetrahydrofuran was purchased from Baxter Chemical and distilled under nitrogen from potassium/benzophenone ketyl. Hexanes was purchased from Baxter Chemical and distilled under nitrogen from sodium/benzophenone ketyl or deoxygenated (by bubbling with nitrogen for at least 20 min) prior to use. Deionized water was taken directly from the tap and deoxygenated by a nitrogen purge prior to use. Chloroacetic acid, 5-chlorovaleric acid, and *trans*-β-hydromuconic acid were purchased from Aldrich Chemical and were deoxygenated (either in vacuo or by purging with nitrogen) prior to use. Triethylamine was purchased from Aldrich Chemical, distilled from P_2O_5 under nitrogen, deoxygenated by three freeze–pump–thaw cycles, and stored under nitrogen in a Teflon sealed Schlenk storage flask. Ethyl chloroformate was purchased from Kodak Chemical and deoxygenated with a nitrogen purge prior to use. Thionyl chloride was purchased from J.T. Baker and used as received.

3.2. Instrumentation and photochemistry

Electronic spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer. Infrared spectra were obtained on either a Nicolet 5DBX FT-IR, a Nicolet DX FT-IR, or on a Nicolet 550 Magna FT-IR controlled by a Gateway 2000 4DX-33V computer running OMNIC software. All ^1H and ^{13}C NMR spectra were recorded on either a General Electric QE-300 or a Varian Unity Inova-300 spectrometer. The photochemical reactions in both solution and the solid-state were carried out as previously described [16–18]. Polymer molecular weights were determined as previously described [18].

3.3. Synthesis of (η^5-$C_5H_5CH_2CH_2NH_2$)

This ligand was synthesized using a modification of a procedure described by Joubran and Grotjahn.[3] 2-Bromoethylamine hydrobromide (6.20 g, 0.0303 mol) was added to an oven-dried 250 ml round-bottom flask already charged with a stirbar and 80 ml of freshly distilled THF, fit with a septum, and under nitrogen. This resulted in a clear and white heterogeneous solution. Freshly distilled THF with the volume of 120 ml of was syringed into a second 250 ml round-bottom flask in an ice bath at 0°C, already charged with a stir bar and under nitrogen. To this second round-bottom flask, freshly distilled cyclopentadiene (8.0 ml, 0.0968 mol) at 0°C and under nitrogen was also added via syringe. This solution was then cooled to -78°C in an acetone/dry ice bath. To this solution, *n*-butyl lithium (40.4 ml, 0.0646 mol) was added via syringe. This reaction mixture was then stirred for 20 min, at which time it was added via cannula to the solution of 2-bromoethylamine hydrobromide in THF. The combined reaction solution was then stirred at 4°C for 48 h, during which time the reaction color turned from clear and white to dark orange-brown. Next, the reaction solution was added via cannula to an 800 ml separatory funnel and diluted with 200 ml deoxygenated diethyl ether. (The ether was deoxygenated by a nitrogen purge.) The organic reaction mixture was then washed with 2 × 100-ml deoxygenated H_2O and then dried over $MgSO_4$. The product was isolated in vacuo as a clear-yellow oil (2.56 g, 78%). ^1H NMR ($CDCl_3$): δ 6.44, 6.29, 6.23, 6.08 (m (br), 3H, *Cp*$CH_2CH_2NH_2$); 2.98 (d, 2H, *Cp*C

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[2] Note that oxo complexes form in the solution phase reactions of $Cp_2Mo_2(CO)_6$ with O_2. See Refs. [34,35].

[3] C. Joubran, D. Grotjahn, Department of Chemistry, Arizona State University, Tempe, AZ 85287-1604, personal communication.

$H_2CH_2NH_2$); 2.90, 2.88 (t, 2H, $CpCH_2CH_2CH_2NH_2$); 2.57, 2.55, 2.53, 2.51 (m, 2H, $CpCH_2CH_2NH_2$); 1.25 (s (br), 2H, $CpCH_2CH_2NH_2$).

3.4. Synthesis of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$

The synthesis of $[(CpCH_2CH_2NH_3^+)Mo(CO)_3]_2[NO_3^-]_2$ has been previously described [17]. Described here is a modified synthesis, somewhat easier, which gave the product with a similar yield and purity. All of the following manipulations were performed in the dark and under nitrogen, unless otherwise noted. A 500 ml three-neck round-bottom flask, already charged with a stir bar and cyclopentadienylethylamine (2.56 g, 23.45 mmol), was charged with 100 ml of freshly distilled THF, and cooled to −78°C in an acetone/liquid nitrogen bath. To this solution, *n*-butyl lithium (6.0 ml, 8.4 mmol) was added via syringe, after which the reaction mixture changed color to pinkish-brown while being stirred for 30 min. The reaction mixture was then allowed to warm to −20°C, after which $Mo(CO)_6$ (7.18 g, 27.2 mmol) was added to the deprotonated-ligand solution. The reaction mixture was then heated to 55°C (reflux) for 48 h, after which it was cannulaed into a deoxygenated aqueous solution of $Fe(NO_3)_3 \cdot 9\ H_2O$ (made by dissolving $Fe(NO_3)_3 \cdot 9\ H_2O$ (7.8 g, 19.3 mmol) in 170 ml distilled water in a 300 ml round-bottom flask and degassed by purging with nitrogen for 20 min) resulting in the formation of a deep-red, heterogeneous solution. The reaction mixture was cooled to 0°C in an ice bath and kept under N_2 for 48 h. The reaction mixture was then filtered *in air* (but in the dark) through a 150 ml glass filter-frit, resulting in the isolation of a deep-red solid material. The product was then dried *in air* for 48 h before being brought into the drybox. In the drybox, the product in the frit was extracted with approximately 5 × 20-ml MeOH, after which the combined extracts were concentrated in vacuo to approximately 20 ml. Next, approximately 80 ml of diethyl ether was layered on top of the MeOH, the flask was fitted with a septum and placed into the drybox freezer for 48 h. The product was isolated as a fine red precipitate via suction–filtration in a 60 ml medium porosity frit then dried in vacuo for 2 h. Analytically pure product was obtained (0.777 mg, 7%). ^1H NMR (DMSO-d_6): δ 7.79 (s (br), 6H, $CpCH_2CH_2NH_3$); 5.72, 5.61, 5.29 (m (br), 4H, *Cp*$CH_2CH_2NH_3$); 2.96, 2.94, 2.91 (t, 4H, $CpCH_2CH_2NH_3$); 2.67, 2.64 (t, 4H, $CpCH_2CH_2NH_3$). IR (KBr) cm^{-1}: 3107 (m), 2923, (m) (1° amine salt); 2016 (m), 1961 (vs), 1914 (vs), 1886 (vs) (ν(C≡O)); 1389 (s), 1348 (s) (amine).

3.5. Synthesis of $CH_3CH_2OC(O)OC(O)CH_2Cl$

Chloroacetic acid (13.3 mg, 0.141 mmol) was placed into an oven-dried Schlenk flask already charged with a stir bar. The flask was fit with a septum and purged with N_2 for 40 min while stirring. Freshly distilled THF with a volume of 10 ml was then added via syringe. To this clear and colorless solution, Et_3N (50 μl, 0.359 mmol) was added via syringe. The solution was then cooled to 0°C in an ice bath for 5 min, at which time ethyl chloroformate (25 μl, 0.261 mmol) was added via syringe. The reaction mixture immediately turned from clear and colorless to cloudy and white. The solution was stirred for 40 min before it was allowed to react in situ with $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$.

3.6. Synthesis of **2**, $[(CpCH_2CH_2N(H)C(O)CH_2Cl)Mo(CO)_3]_2$

All of the following manipulations were performed in the dark, and under nitrogen, unless otherwise noted. In the drybox, $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ (48.8 mg, 0.069 mmol) was placed into an oven dried Schlenk flask, already charged with a stir bar and fitted with a septum. The flask was then brought out of the drybox. The Schlenk flask was put under N_2, and 20 ml of freshly distilled THF were added via syringe. The heterogeneous, red solution was stirred for 5 min, at which time Et_3N (50 μl, 0.359 mmol) was added via syringe, which resulted in the formation of a homogenous, red solution. The dimer solution was then stirred for 15 min, after which it was cooled to 0°C, in an ice bath. After 35 min, the bis-mixed anhydride was added in situ via cannula to the amine dimer. The Schlenk flask which had contained the mixed anhydride was rinsed with 10 ml THF which was cannulaed into the reaction mixture. The reaction mixture was stirred for 5 min at 0°C, after which the ice bath was removed. The reaction was then stirred for 22.3 h, after which it was concentrated in vacuo to 5 ml of a clear-red solution, put under N_2, and cannulaed into 100 ml de-ionized, deoxygenated (by bubbling with N_2 for 90 min) water at 0°C, resulting in the immediate formation of a cloudy-red solution. The cloudy-red solution was filtered *in air* through a fine porosity glass filter-frit to separate a red solid from a clear and colorless filtrate. The red solid was dried *in air* for 18.4 h then transferred into the drybox. The red product was dissolved with 2 × 20-ml and 1 × 10-ml THF and filtered through the glass filter-frit it was contained in. This resulted in a clear-red solution, which was concentrated in vacuo to 2 ml and transferred to a round-bottom flask. Hexanes was then layered atop the THF and the round-bottom flask was stoppered and placed into the drybox freezer at −40°C for 48.6 h. The product was isolated by suction–filtration as a fine red precipitate (9.4 mg, 20%; mp 166°C (dec)). ^1H NMR (THF-d_8): δ 7.60 − 7.56 (m (br), 2H, $CpCH_2CH_2N(H)C(O)CH_2$

Cl); 5.41 (s (br), 4H, *Cp*$CH_2CH_2N(H)C(O)CH_2Cl$); 5.21 (s (br), 4H, *Cp*$CH_2CH_2N(H)C(O)CH_2Cl$); 3.96 (s, 4H, $CpCH_2CH_2N(H)C(O)CH_2Cl$); 3.37, 3.35, 3.33, 3.31 (m, 2H, $CpCH_2CH_2N(H)C(O)CH_2Cl$); 2.63, 2.61, 2.59, 2.57 (m, 4H, $CpCH_2CH_2N(H)C(O)CH_2Cl$). IR (KBr)cm^{-1}: 3305 (m), 3093 (w) (free N–H); 2016 (m), 1948 (vs), 1921 (sho, vs), 1907 (vs)(ν(C≡O)); 1689 (m), 1655 (m) (amide I); 1539 (m), 1266 (m) (amide II); 830 (m) (C–N str.). UV–Vis (THF): λ nm, ε M^{-1} cm^{-1}; 505 (1548); 391 (15,038). Anal. Calc. for $C_{24}H_{22}N_2O_8Mo_2Cl_2$:C, 39.53; H, 3.04; Found: C, 39.83;H, 3.19.

3.7. Synthesis of $CH_3CH_2OC(O)OC(O)(CH_2)_3CH_2Cl$, an activated mixed anhydride derivative of 5-chlorovaleric acid

A mixed anhydride of $HOC(O)(CH_2)_3CH_2Cl$ was synthesized in an analogous manner to other mixed anhydride compounds. Deoxygenated chlorovaleric acid (15.5 μl, 0.152 mmol) was added via syringe to an oven dried Schlenk flask, under N_2, already charged with a stir bar and 20 ml freshly distilled THF, and fit with a septum. The solution was stirred for 5 min and cooled in an ice bath to 0°C for 5 min. Deoxygenated Et_3N (30 μl, 0.215 mmol) was then syringed into the reaction solution. The solution was stirred for 5 min, after which deoxygenated (by N_2-bubble > 20 min) ethyl chloroformate (15 ml, 0.157 mmol) was added via syringe, resulting in the immediate formation of a turbid solution. The activated mixed anhydride was stirred at 0°C for 110 min before it was reacted in situ with the amine dimer to form **1**.

3.8. Synthesis of **1**, $[(CpCH_2CH_2N(H)C(O)(CH_2)_3CH_2Cl)Mo(CO)_3]_2$

All of the following manipulations were performed in the dark under nitrogen unless otherwise noted. In the drybox, a Schlenk flask already containing a stir bar was charged with $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ (52.1 mg, 0.074 mmol). The flask was fit with a septum and brought out of the drybox. The flask was charged (by syringe) with 20 ml freshly distilled THF resulting in the formation of a heterogeneous-red solution. This solution was stirred for 15 min at which time deoxygenated Et_3N (30 μl, 0.215 mmol) was added via syringe resulting in the formation of a clear-red solution. This solution was stirred for 45 min at which time it was cooled to 0°C in an ice bath. After stirring for an additional 5 min the activated mixed anhydride of 5-chlorovaleric acid was added in situ to the amine dimer **2** via a cannula. The flask which had contained the mixed anhydride was rinsed with 1 × 10-ml freshly distilled THF which was then cannulaed to the reaction mixture. The reaction was stirred for 30 min at 0°C, after which the ice bath was removed and the solution was allowed to warm to room temperature. The reaction mixture was stirred for 18.5 h, after which it was concentrated in vacuo to 10 ml resulting in a clear-red solution. The reaction mixture was then cannulaed into 100 ml de-ionized, deoxygenated (by N_2-bubble for 18.6 h) water at 0°C, resulting in the immediate formation of a cloudy-red solution. The reaction mixture was allowed to set, initially at 0°C, under N_2, for 47.9 h. The product, observed as a red floculent solid in a clear yellow-pink solution, was then isolated, *in air*, via suction–filtration through a medium porosity filter-frit. The product was then dried *in air* for 27.5 h, at which time it was brought into the drybox. In the drybox, the product was dissolved with 3 × 10-ml THF and drawn through the filter-frit. The resulting clear-red solution was then concentrated to 10 ml in vacuo and transferred to a round-bottom flask. Hexanes was then layered on top of the THF. The round-bottom flask was then fit with a septum and placed into the drybox freezer at −40°C for 45.7 h. The product was isolated as a bright-red solid via suction–filtration through a fine porosity filter-frit (28.2 mg, 47%). ^{1}H NMR (THF-d_8:δ 7.10 (s (br), 2H, $CpCH_2CH_2N(H)C(O)(CH_2)_3CH_2Cl$); 5.40 (s(br), 4H, *Cp*$CH_2CH_2N(H)C(O)(CH_2)_3CH_2Cl$); 5.21 (s (br), 4H, *Cp*$CH_2CH_2N(H)C(O)(CH_2)_3CH_2Cl$); 3.56, 3.54, 3.52 (m, 8H, $CpCH_2CH_2N(H)C(O)CH_2(CH_2)_2CH_2Cl$); 3.31, 3.29, 3.27, 3.25 (m, 2H, $CpCH_2CH_2N(H)C(O)(CH_2)_3CH_2Cl$); 2.59, 2.56, 2.54 (t, 4H, $CpCH_2CH_2N(H)C(O)(CH_2)_3CH_2Cl$); 2.12, 2.10, 2.06 (t, 8H, $CpCH_2CH_2N(H)C(O)CH_2(CH_2)_2CH_2Cl$); 1.73 (s (br) 8H, $CpCH_2CH_2N(H)C(O)CH_2(CH_2)_2CH_2Cl$). IR (KBr) cm^{-1}: 3271 (m), 3093 (w) (free N–H); 2009 (m), 1941 (vs), 1893 (vs) (ν(C≡O)); 1641 (m) (amide I); 1559 (m), 1239 (m), (amide II); 836 (m) (C–N str.). UV–Vis (THF): λ nm, ε M^{-1} cm^{-1}; 506 (1951); 392 (19,032). Anal. Calc. for $C_{30}H_{34}N_2O_8Mo_2Cl_2$: C, 44.30; H, 4.21; Found: C, 44.47; H, 4.16.

3.9. Synthesis of 3,4-dichlorohexanedioic acid; $HOC(O)CH_2CH(Cl)CH(Cl)CH_2C(O)OH$

The synthesis of 3,4-dichlorohexanedioic acid was carried out by using a modification of a literature procedure [32]. An oven-dried 250 ml round-bottom flask already deoxygenated and charged with a stir bar was fit with a reflux condenser. *trans*-β-Hydromuconic acid (973.6 mg, 6.755 mmol) was then added to the round bottom under a nitrogen counter-flow, after which the set-up was evacuated for 2 min with stirring. The reaction apparatus was then put under nitrogen and 2 × 50-ml freshly distilled THF was added via syringe, at which time all of the white solid diacid dissolved. To this solution, thionyl chloride (500 μl, 6.855 mmol) was added via syringe. The clear and colorless reaction mixture was heated to reflux for 9.3 h resulting in a clear-yellow solution, which was subsequently stirred for 15.5 h at room temperature. The solution was concentrated in vacuo to yield a yellow oil which was then partially dissolved in 50 ml $\mathrm{Et_2O}$ to give a heterogeneous yellow solution. This solution was then extracted with 3×30-ml saturated $\mathrm{NaHCO_3}$ and allowed to dry in air for 70.3 h resulting in a clear-yellow liquid. Next, the product was completely dissolved in THF, dried over MgSO, and filtered through a #4 Whatman filter paper into an oven-dried 100 ml round-bottom flask already charged with a stir bar. The solution was concentrated in vacuo resulting in a yellow solid. The solid was dissolved in 2×5-ml THF and transferred to a tarred, oven-dried 50 ml round-bottom flask charged with a stir bar. Volatiles were removed in vacuo to yield a yellowish-white pasty solid (164.1 mg, 11.3% mass recovery). ^{1}H NMR (MeOH-d_4): δ 4.08 (m, 2H, $\mathrm{(HOC(O)CH_2C}H\mathrm{Cl)_2}$); 3.56, 3.55, 3.54 (m, 4H, $\mathrm{(HOC(O)C}H_2\mathrm{CHCl)_2}$). ^{13}C NMR (MeOH-$d_4$): δ 128.26 (s, $\mathrm{(HOC(O)CH_2}C\mathrm{HCl)_2}$); 127.44 (s, $\mathrm{(HOC(O)CH_2}C\mathrm{HCl)_2}$); 39.10 (s, $\mathrm{(HOC(O)}C\mathrm{H_2CHCl)_2}$).

3.10. Synthesis of $(CH_3CH_2OC(O)OC(O)CH_2CHCl)_2$, *an activated mixed anhydride derivative of 3,4-dichlorohexanedioic acid*

The activated mixed anhydride $\mathrm{(CH_3CH_2OC(O)OC(O)CH_2CHCl)_2}$ was synthesized in an analogous manner to other mixed anhydride compounds. An oven-dried 50 ml round-bottom flask, already containing a stir bar, was charged with the yellow–tan solid 3,4-dichlorohexanedioic acid (164 mg, 0.763 mmol). The flask containing the solid diacid was then fit with a septum and evacuated for 1 min to deoxygenate the flask. The flask was then put under nitrogen and 20 ml of freshly distilled THF was added via syringe, resulting in a clear-yellow solution. The reaction mixture was then allowed to cool to 0°C in an ice bath for 10 min, with stirring. Deoxygenated triethylamine (250 μl, 1.79 mmol) was then syringed into the mixture, while stirring at 0°C, and under nitrogen, for 40 min. Deoxygenated ethyl chloroformate (150 ml, 1.55 mmol) was then added via syringe to the reaction flask at which time the reaction mixture turned from clear-yellow to cloudy and yellow. The reaction mixture was then stirred for 60 min during which time the solution continued to change color from cloudy yellow–green to cloudy green–brown. The activated mixed anhydride was not characterized, but rather its formation inferred by the formation of a cloudy solution, which was then reacted in situ with the deprotonated ammonium dimer to form **3**.

3.11. Synthesis of polyamide **3**, $[-C(O)N(H)CH_2CH_2Cp)Mo(CO)_3Mo(CO)_3\text{-}(CpCH_2CH_2N(H)C(O)CH_2(CHCl)_2CH_2-]_n$

All of the following manipulations were performed in the dark, and under nitrogen, unless otherwise noted. In the drybox, an oven round-bottom flask, already containing a stir bar, was charged with $[(\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2NH_3^+})_2\mathrm{Mo_2(CO)_6}][\mathrm{NO_3^-}]_2$ (58.1 mg, 0.083 mmol). The flask was fitted with a septum, removed from the drybox, and purged with nitrogen, for 2 h. Freshly distilled THF with a volume of 20 ml of was syringed into the reaction round-bottom flask, while the contents was stirred in the dark, resulting in a heterogeneous-red solution. Deoxygenated triethylamine (40 ml, 0.287 mmol) was then added via syringe, resulting in a homogenous-red solution. The reaction solution was then stirred for 15 min while it was cooled to 0°C in an ice bath. Next, the bis-mixed anhydride was added to the amine dimer via cannula in one aliquot. The ice bath was removed from under the reaction flask and allowed to warm to room temperature. The reaction was stirred, in the dark, under nitrogen for 2.5 h at which time it was concentrated in vacuo. Seventy milliliters of ice cold deoxygenated water was added via cannula to the red oil left in the round-bottom flask. This solution was kept under nitrogen, in the dark for 49 h, at which time it was isolated in air in a 60 ml course porosity filter-frit. The product remaining in the round-bottom and contained in the filter-frit were dried *in air* for 16.5 days, then brought into the drybox. In the drybox, the oily red material both in the round-bottom and in the frit were dissolved in THF and drawn through the frit which contained part of the material. The resulting clear-red solution was transferred to an Erlenmeyer flask and concentrated in vacuo to 2 ml. Hexanes were layered atop and the Erlenmeyer flask containing solution was stoppered and placed into the drybox freezer at -40°C for 26 h. The product was isolated as a dark red oily solid after filtration through a 60 ml medium porosity filter-frit. (137.1 mg, 73.8% mass recovery) ^{1}H NMR (THF-d_8): 7.00 (s (br), 2H, $\mathrm{CpCH_2CH_2N(}H\mathrm{)C(O)CH_2CHCl}$–); 5.400 (s (br), 4H, $Cp\mathrm{CH_2CH_2N(H)C(O)CH_2CHCl}$–); 5.21 (s (br), 4H, $Cp\mathrm{CH_2CH_2N(H)C(O)CH_2CHCl}$–); 4.03, 4.01, 3.99, 3.96 (m, 2H, $\mathrm{CpCH_2CH_2N(H)C(O)CH_2C}H\mathrm{Cl}$–); 3.24, 3.21, 3.19, 3.17(m, 4H, $\mathrm{CpCH2C}H_2\mathrm{N(H)C(O)CH_2CHCl}$–); 2.59, 2.56, 2.54(t, 4H, $\mathrm{CpC}H_2\mathrm{CH_2N(H)C(O)CH_2CHCl}$–); 2.49, 2.45(d, 4H, $\mathrm{CpCH_2CH_2N(H)C(O)C}H_2\mathrm{CHCl}$–). IR (KBr) cm^{-1}: 3107 (w) (free N–H); 2016 (m), 1955 (vs), 1900 (vs) (υ(C≡O)); 1641 (m) (amide I); 1471 (m), 1266 (m), (amide II); 823 (m) (C–N str.). UV–Vis (THF): λ nm; 505, 392. Anal. Calc. for $\mathrm{C_{26}H_{24}N_2O_8Mo_2Cl_{1.5}}$: Cl, 7.21 Found: Cl, 6.72.

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