

Systematic Study on Reaction Dynamics of Furan, Maleimide and Anthracene for responsive polymer applications

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We developed systematic and basic rules of reaction dynamics of three model compounds, 2-MethylFuran, N-MethylMaleimide, and anthracene across the range of temperatures and UV light to establish the selective rule of the Diels-Alder (DA) reaction and photodimerization among them. Analysis of results was investigated through H-NMR using d-chloroform as solvent. Due to its efficient thermal stability, those three compounds were selected in this work. This study suggests a basic reference to improve the control of crosslinking reactions among them which can further induce the change of polymer properties. Through this work, it was shown that both DA reactions of furan-maleimide and anthracene-maleimide were carried out at low temperatures (30°C, 40°C, and 50°C) at a similar rate. On the other hand, at 120°C retro-Diels Alder reaction only between furan and maleimide occurred. Furan and maleimide bonds were broken; while anthracene was linked with maleimide even more than it was at the low temperatures. Photodimerization of anthracene under UV light ($\lambda=365\text{nm}$) showed very low concentration ($\sim 6\%$). This was because of the low solubility of the solvent we used. Therefore it was difficult to obtain the high concentration of anthracene dimers on H-NMR analysis. These findings can further influence the polymer-scale research among these compounds to accomplish the versatile responsive polymer chemistry.

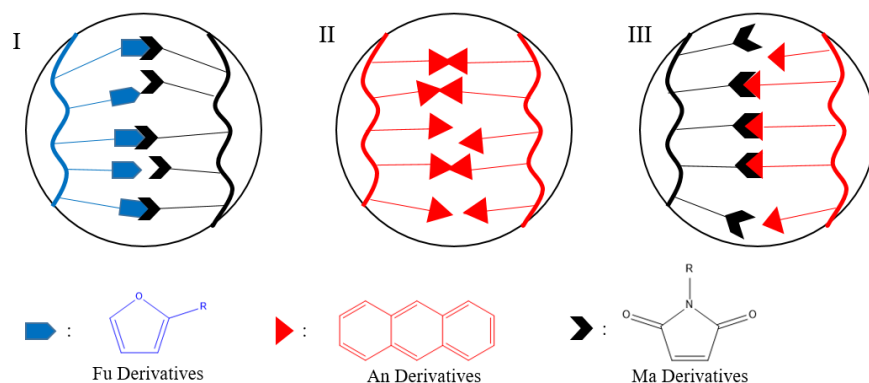
Introduction

Over the last decade, scientists have brought attention to the use of rapid reactions that satisfy the three major factors of an ideal synthesis: efficiency, versatility, and selectivity [1]. The studies on reactions which can achieve these factors have been extensively explored, known as “click” reactions [2]. Diels Alder (DA) reaction is one of the most frequently used click reactions due to its variable substrate scope, high yields and also its thermo-reversibility [3]. The DA reaction involves [4 + 2] cycloaddition of a diene and a dienophile, requiring very low energy and mild conditions [4]. Thus DA reactions allow for the feasible access to the reversibility in a range of temperatures in many cases [5]. This leads to a reaction that can be applied to a broader range of polymers [4]. Especially the dynamics of covalently thermo-reversible networks, resulting from the DA reaction, can control the association and dissociation of dynamic covalent polymers within a defined conditions range. Therefore they are excellent candidates for recyclable, self-healing and drug-release materials [6][7].

From the many DA pairs that have been studied, furan (Fu) and maleimide (Ma) have received plenty of attention [8]. Its low coupling and high decoupling temperatures, in other words its efficient thermal stability, make furan-maleimide widely used reversible polymer cross-linking [3][8]. To elaborate further on it, furan functionalized polymer and maleimide-containing polymer (Figure 1a(i),b(i)) can be crosslinked at 50°C via DA reaction. Upon heating up to 120°C, the crosslinked polymer was reversed to the starting

material [9][10]. Besides the use of Fu as diene in the thermoreversible DA reaction, anthracene derivatives (An) can also be another option to use as diene because it shows higher thermal stability with Ma than Fu-Ma linkage (Figure 1 a (iii), b (iii)) [11]. Therefore much research on transform under thermodynamic control of An-Ma DA reaction was explored previously, demonstrating the favorable and stable An-Ma links, which can be cleaved by heating at 200°C [3][11]. Anthracene groups (Figure 1 a (ii), b (ii)) can experience efficient cycloaddition to produce anthracene dimers under UV light ($\lambda > 300\text{nm}$) or sunlight. These dimers can reversibly dissociate after heating with relatively high temperatures of irradiation (170°C) or with high energy UV light ($\lambda < 300\text{nm}$) [12][13].

a.



b.

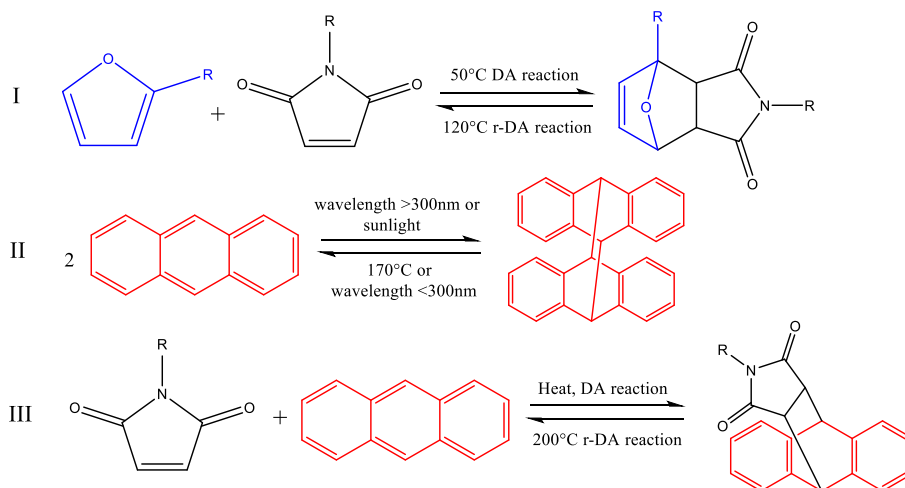


Figure 1 | Polymer system of FuMa, AnAn, and AnMa with different pathways to react. a) Scheme of hermo- and photo-reversible crosslinked polymers (i) thermoreversible crosslinked polymers by of Fuand Ma moieties (ii) Photodimerization of Anthracene dimer under UV light (iii) Macromolecular metamorphosis via stimulus-induced transformations of polymer architecture between Anthracene and Maleimide. b) Reaction Scheme of (i)(ii) (iii)

Here we performed the reaction in NMR tube with in d-chloroform and analyze the result directly with H-NMR spectroscopy. Since this reaction was carried out under controlled temperature up to 120°C, NMR tube had to be sealed to prevent the evaporation of the solvent which boils at 61.2°C. It was important to

work systematically and clearly to find out how Fu, Ma and An react with each other at a certain temperature. The experiments were conducted as follow:

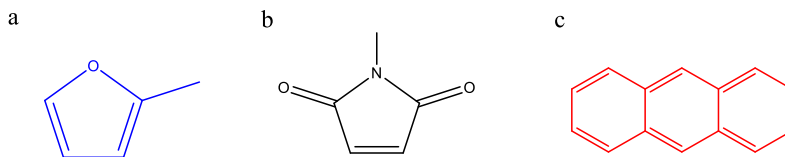
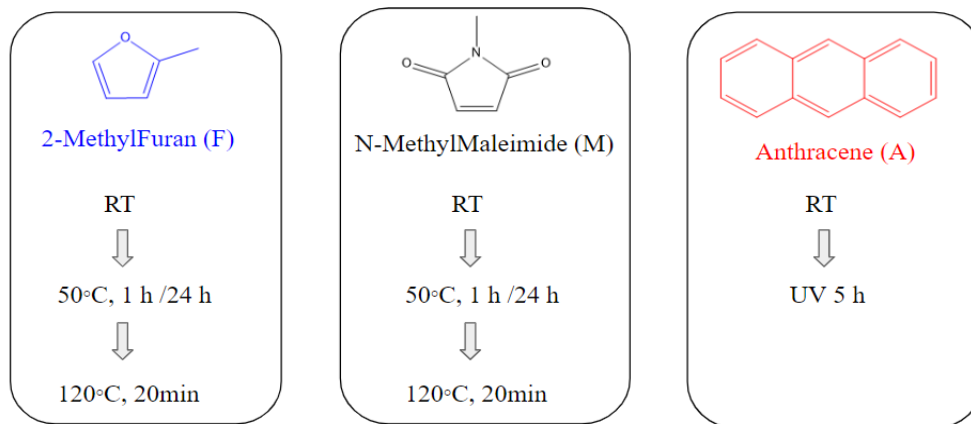


Figure 2 | Model compounds. a) 2-MethylFuran b) N-MethylMaleimide c) Anthracene

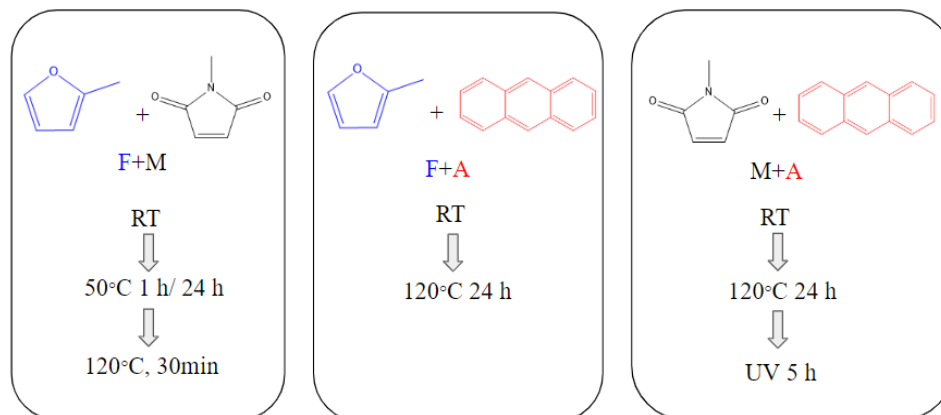
Experimental

The strategy we decided to explore in this work is to perform the reaction in NMR tube with a solvent of d-chloroform and analyze the result directly with H-NMR spectroscopy. Since this reaction was carried out under controlled temperature up to 120°C, NMR tube had to be sealed to prevent the evaporation of the solvent which has the boiling point of 61.2°C. It was important to work systematically and clearly to find out how Fu, Ma and An react with each other at a certain temperature. Here is the flowchart that will show how we organized the experiment.

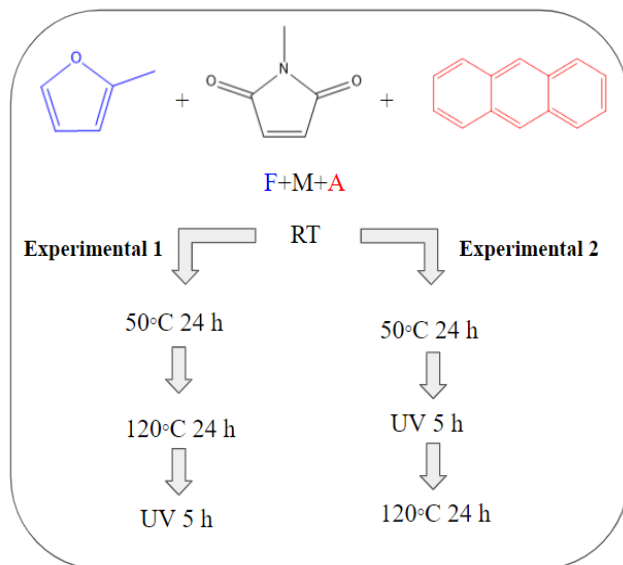
a. Reference for Model Compounds



b. Reference for Reacted Compounds in pairs



c. Reacted All Model Compounds Together



d. Reactivity of FuAn and MaAn at low temperature and photodimerization of Anthracene for a long time

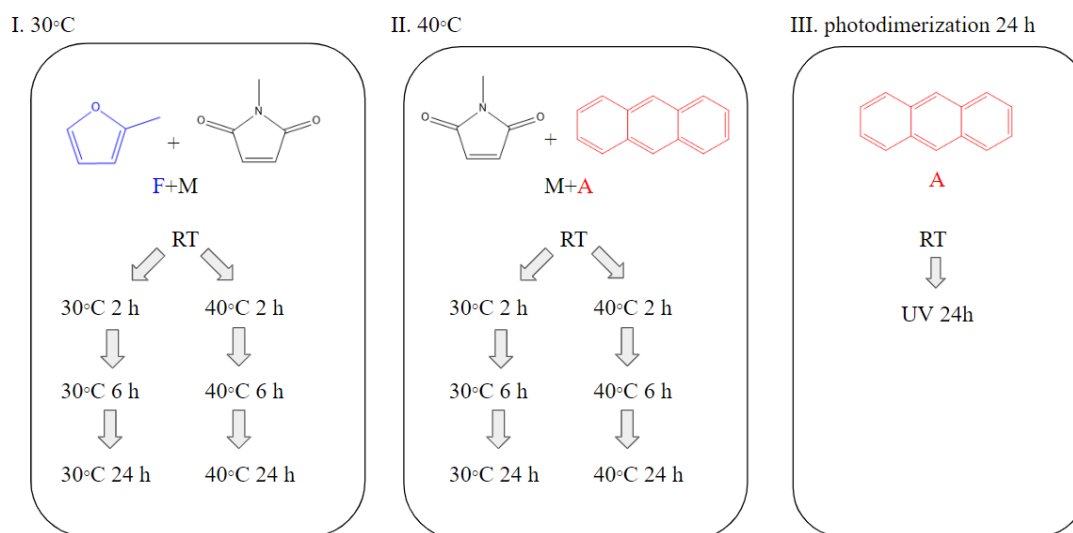


Figure 3 | Flowchart of methodology. a) Reference for Model Compounds. H-NMR of three model compounds at different temperatures. **b) Reference for Reacted Compounds in pairs.** H-NMR of model compounds combinations of two at different temperatures with 1:1 mole ratio. **c) Reacted All Model Compounds Together.** H-NMR of model compounds mixed all in one with 0.6:2:3.6=F:M:A mole ratio. **d) Reactivity of FuAn and MaAn at low temperature and photodimerization of Anthracene for a long time.** Extra experimental of F+A and M+A at lower temperatures (30°C and 40°C), and photodimerization of anthracene after 24 h reaction time.

We first investigated the three model compounds at different temperatures for the free compounds reference (Figure 3a). Then the paired compounds with mole ratio of 1:1 were reacted for the reaction reference (Figure 3b). Subsequently to figure out the precise rules among these three model compounds as our final

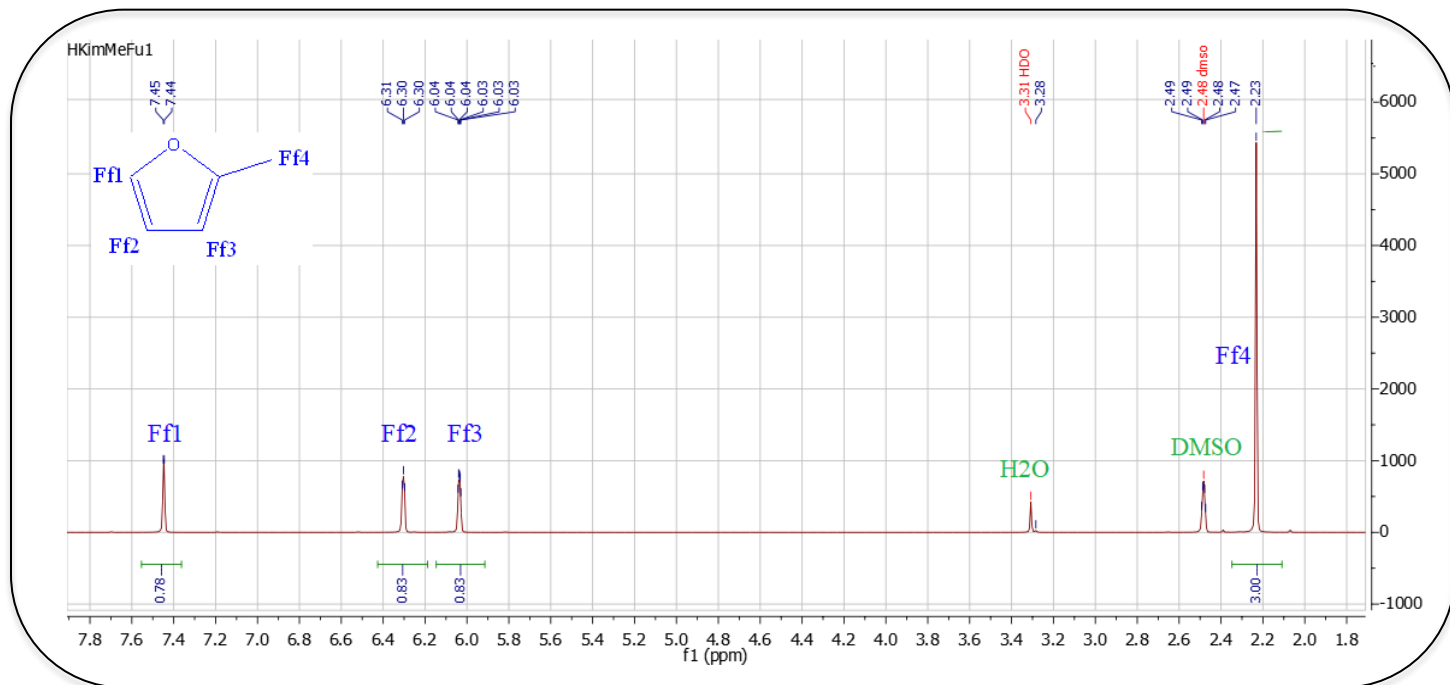
goal, all three model compounds were added up in two different NMR tubes with 0.6:2:3.6=F:M:A mole ratio each. Both tubes underwent different routes (Figure 3c): RT-50°C-120°C-UV ($\lambda = 365\text{nm}$) and RT-50°C-UV ($\lambda = 365\text{nm}$) -120°C respectively. As extra experimentals (Figure 3d), it was necessary to figure out the reaction speed between FuAn reaction and MaAn reaction at lower temperature. Therefore the reaction took place at 30°C and 40°C, and the spectra were recorded at these time intervals; 0h, 2h, 6h, and 24h. Furthermore, we studied the efficiency of the dimerization of anthracene after 24 hours reaction time.

Results & Discussion

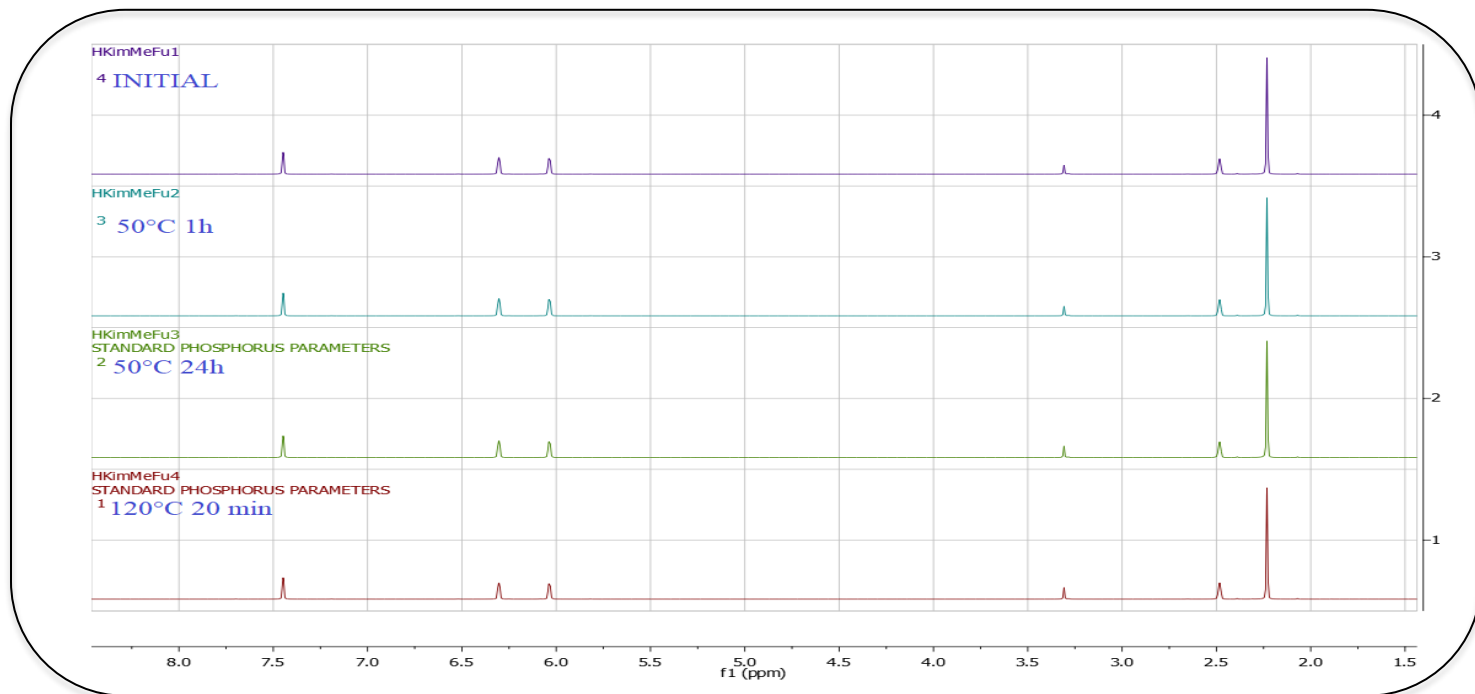
Figure 4 shows the H-NMR interpretations of three model compounds: Fu, Ma and An, at different reaction times and temperatures. Figure 4a, b demonstrates the Fu and Ma do not decompose or get oxidized in the range of room temperature until 120 °C. Only integration of water gets higher because the chemical was exposed to the air longer and longer as time goes by. In the An case (Figure 4c), it was successful to dimerize the anthracene under UV light ($\lambda = 365\text{nm}$), but during the anthracene dimerization, the reaction brought out the byproduct of anthracene endoperoxide [14]. It is noted that; however, the presence of byproduct is very small and does not affect the further reaction. Therefore the presence of anthracene endoperoxide can be neglected to set the basics through Fu, Ma and An chemistries.

a. 2-MethylFuran

a- i. Initial at RT

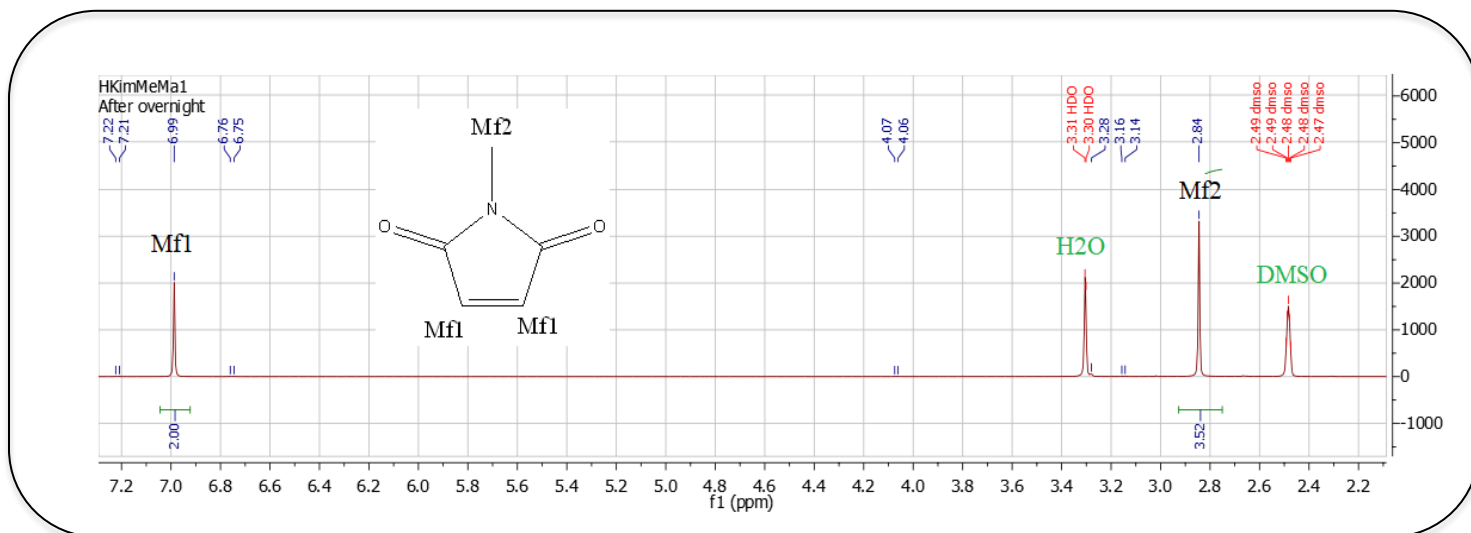


a- ii. 50°C 1h/ 24h and 120°C 20 min

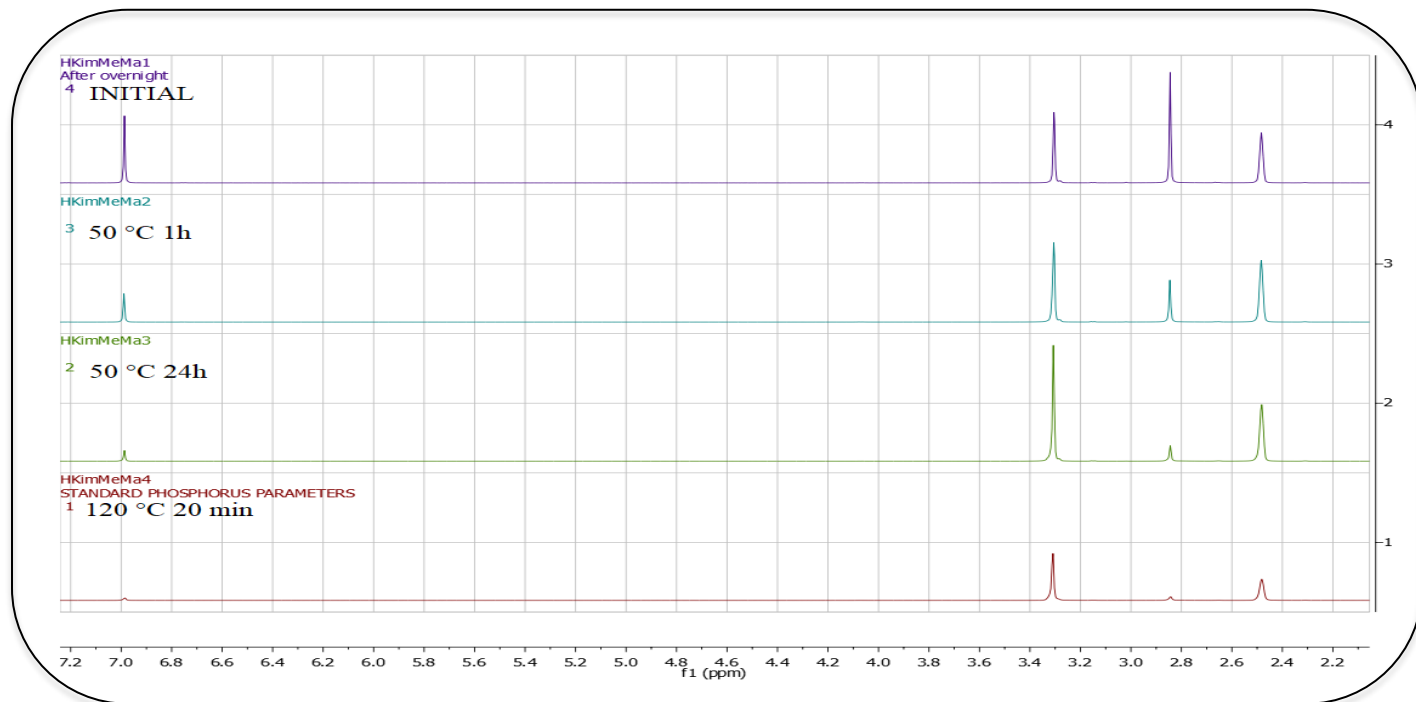


b. N-MethylMaleimide

b- i. Initial at RT

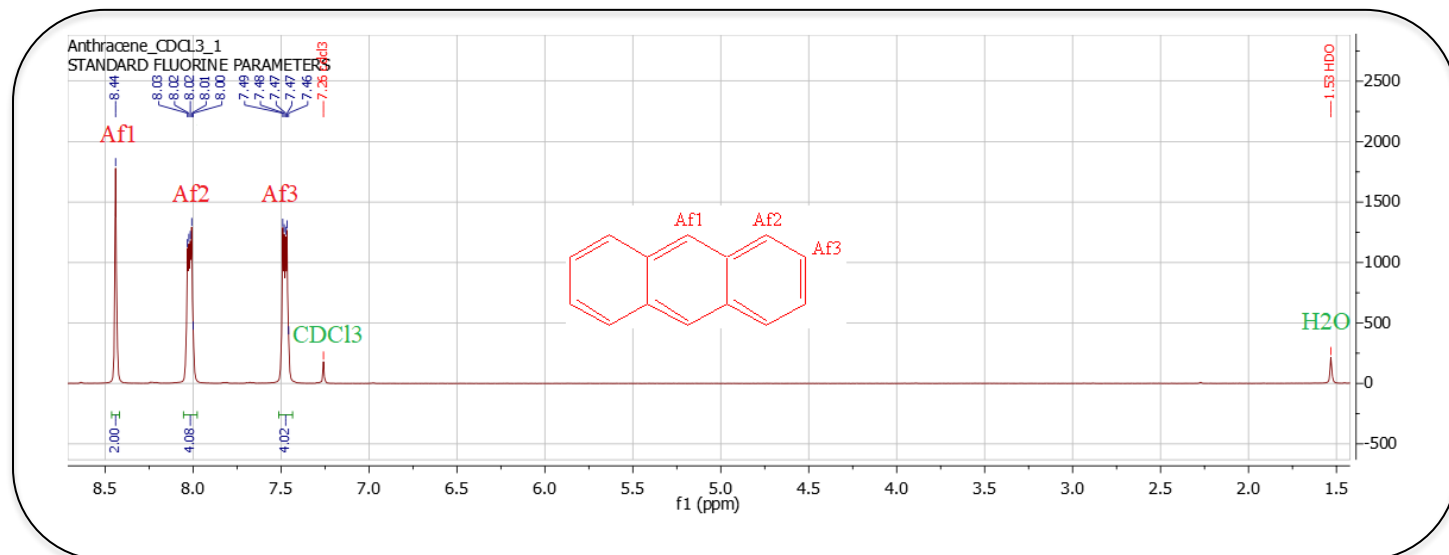


b- ii. 50 °C 1h/ 24h & 120 °C 20min



c. Anthracene

c- i. Initial at RT



c - ii. UV light 5 h reaction

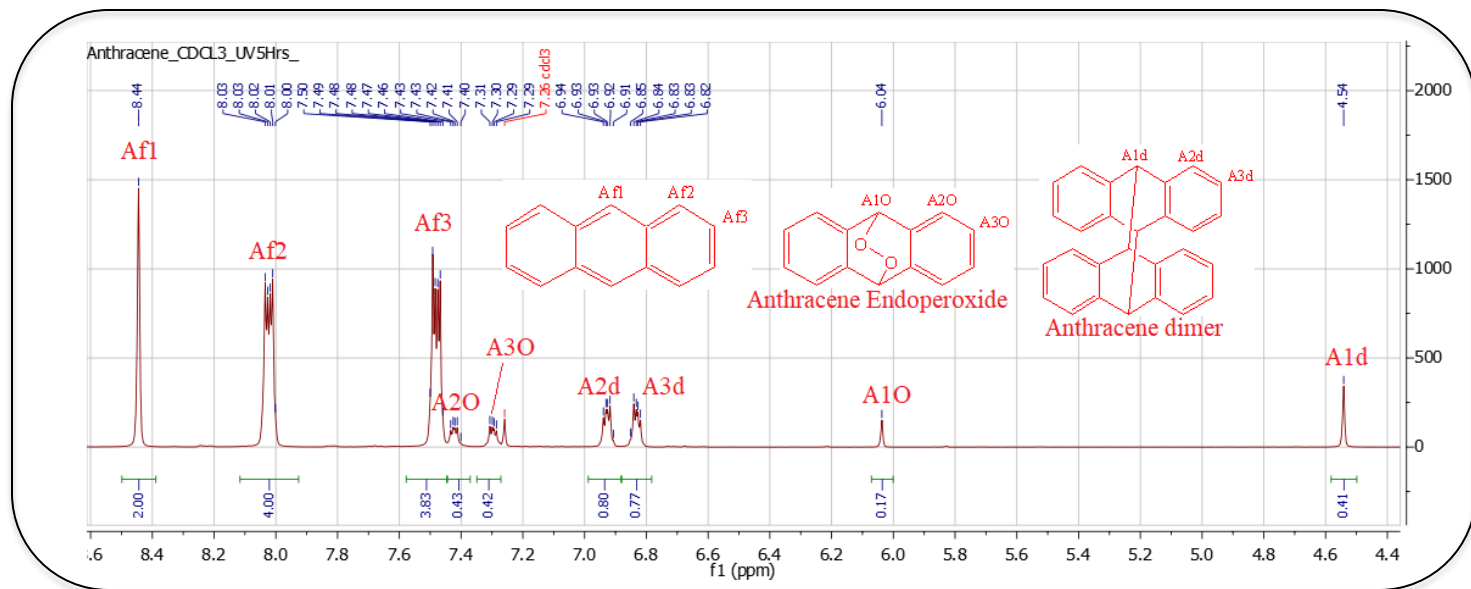
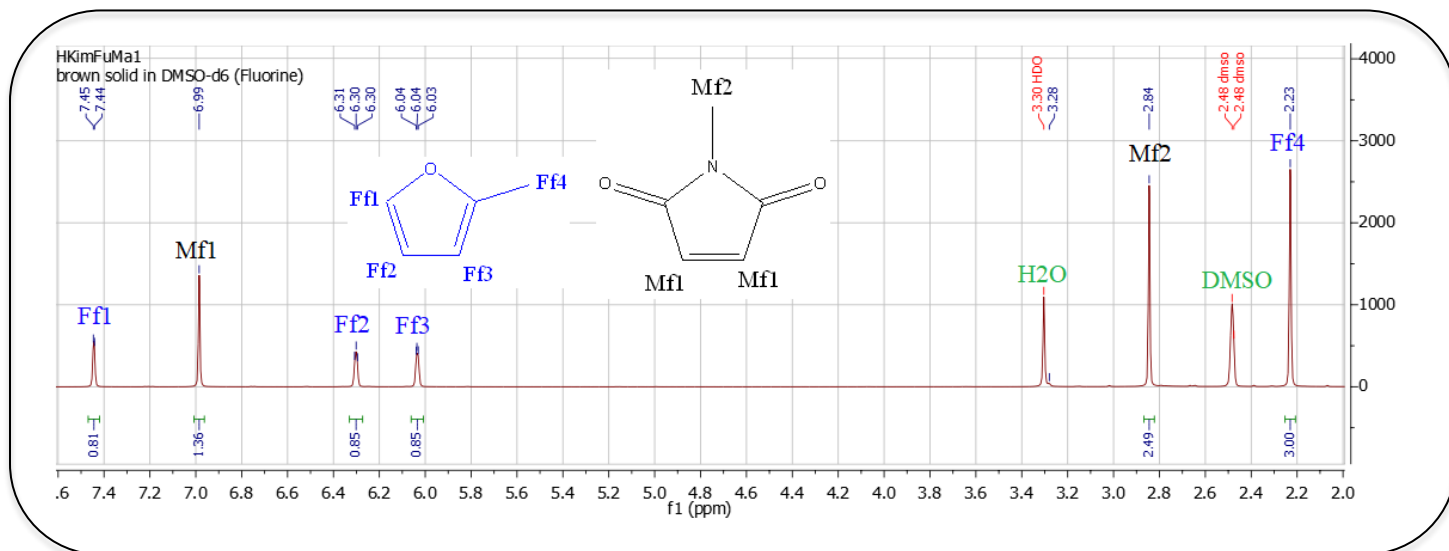


Figure 4 | H-NMR interpretations of reference for model compounds (figure 3a). a) 2-MethylFuran b) N-MethylMaleimide c) Anthracene

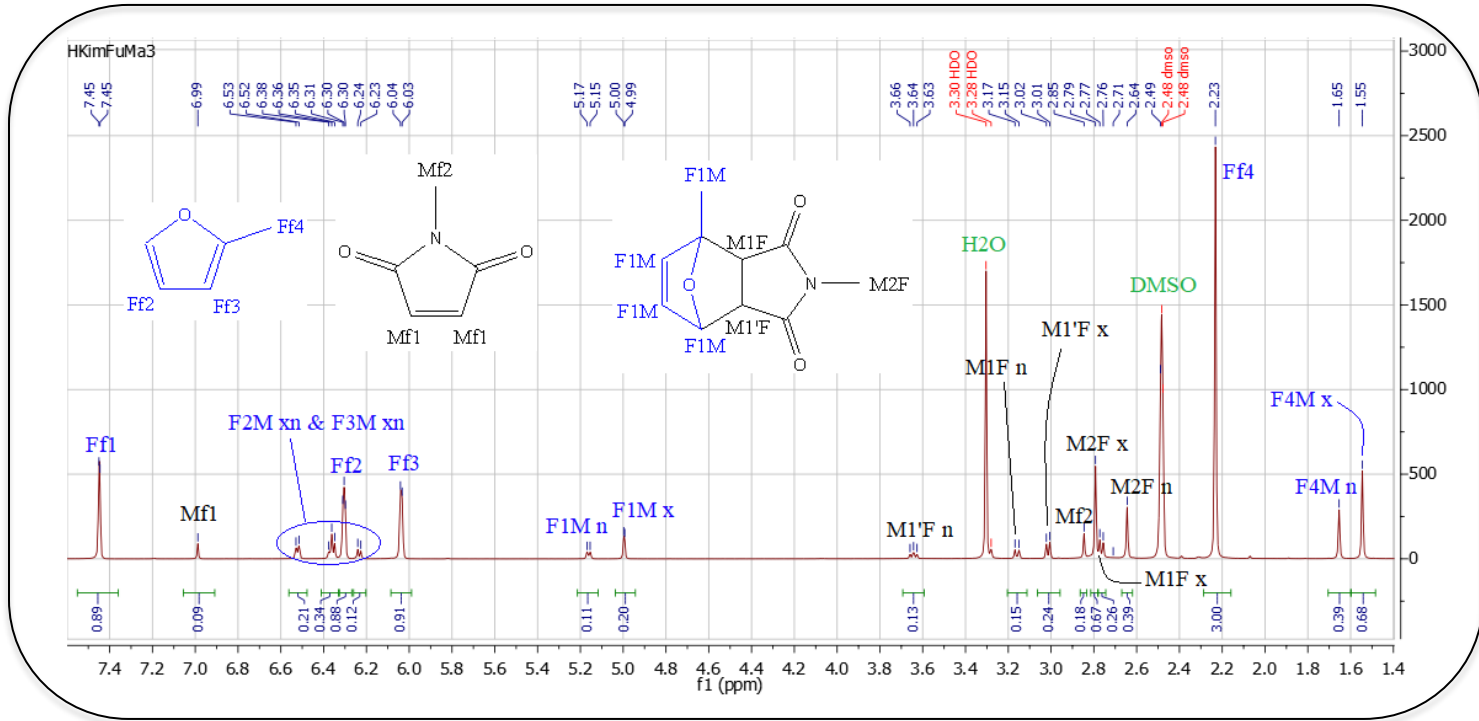
Based on Figure 5a, it was observed that Fu and Ma are linked at 50°C and delinked at 120°C via DA reaction. Disassociation between Fu and Ma is noticed by the increase of integral of Fu free and Ma free and decrease of endo, exo adduct. Figure 5b shows no reactions between Fu and An at any temperatures that were explored. Figure 5c indicates the reaction between Ma and An. It was proved that at 120°C, Ma and An underwent the DA reaction as expected. After being exposed to UV for 5 hours, free anthracene was dimerized with very low concentration (Figure 5c iii). This little formation of anthracene dimer will be discussed in the further discussion part.

a. Fu+Ma

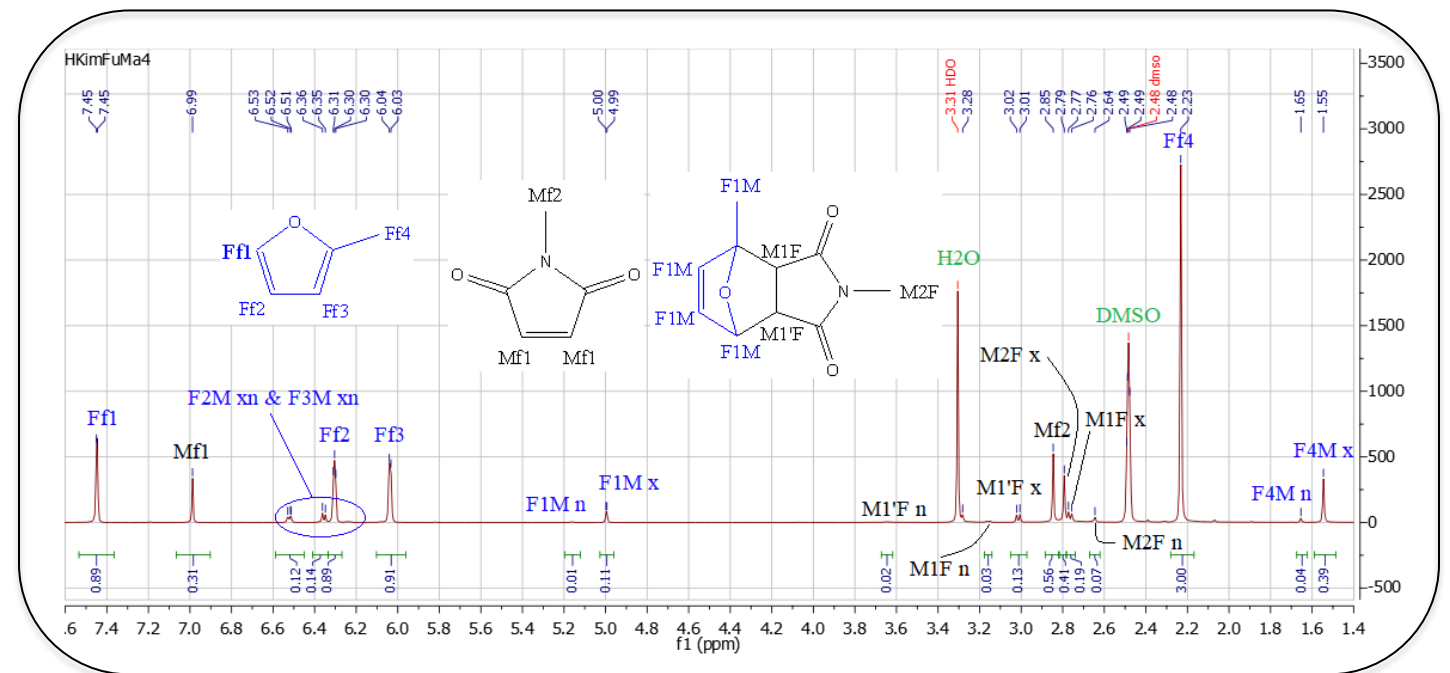
a- i. Initial at RT



a- ii. 50 °C 24h

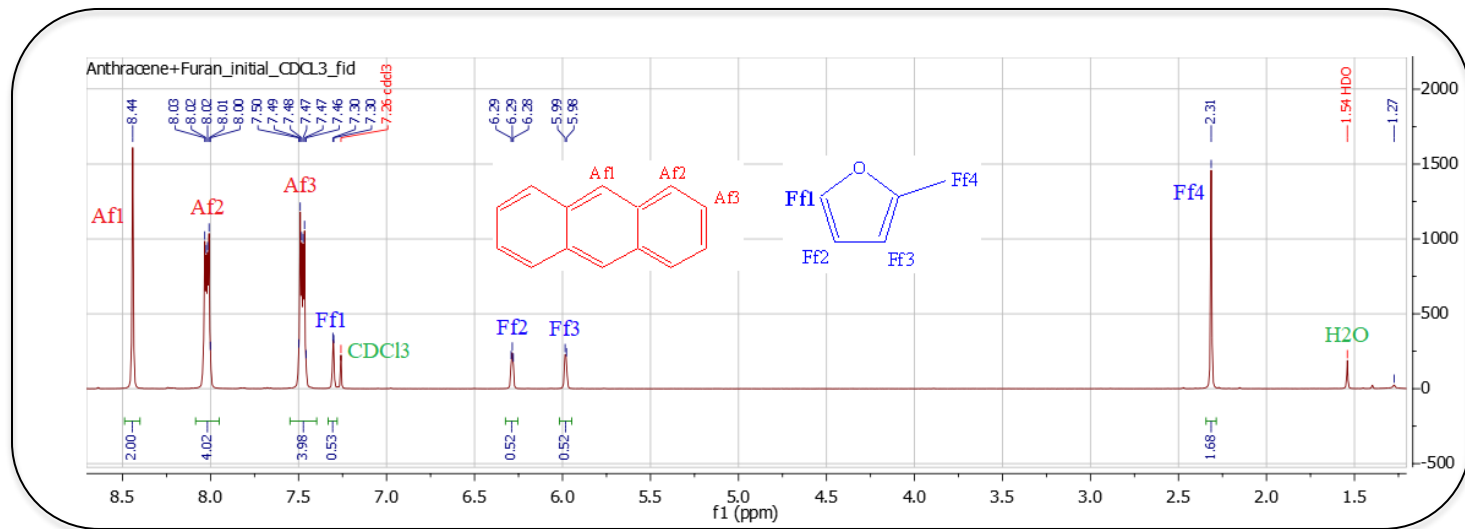


a- iii. 120 °C 30min

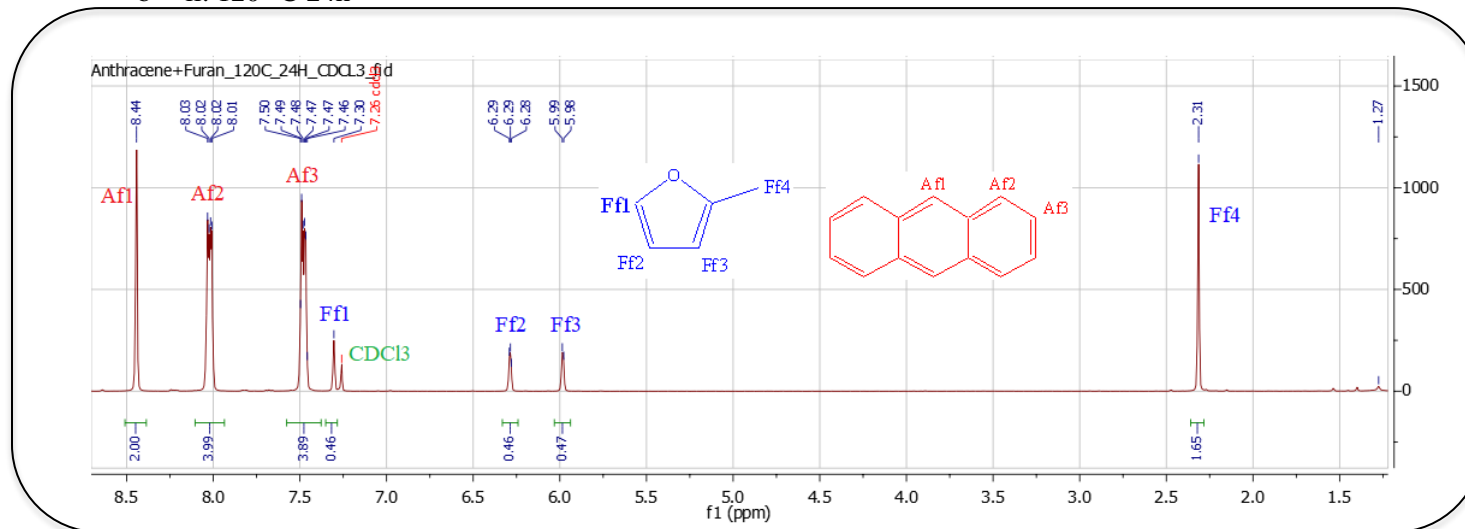


b. Fu+An

b- i. Initial at RT

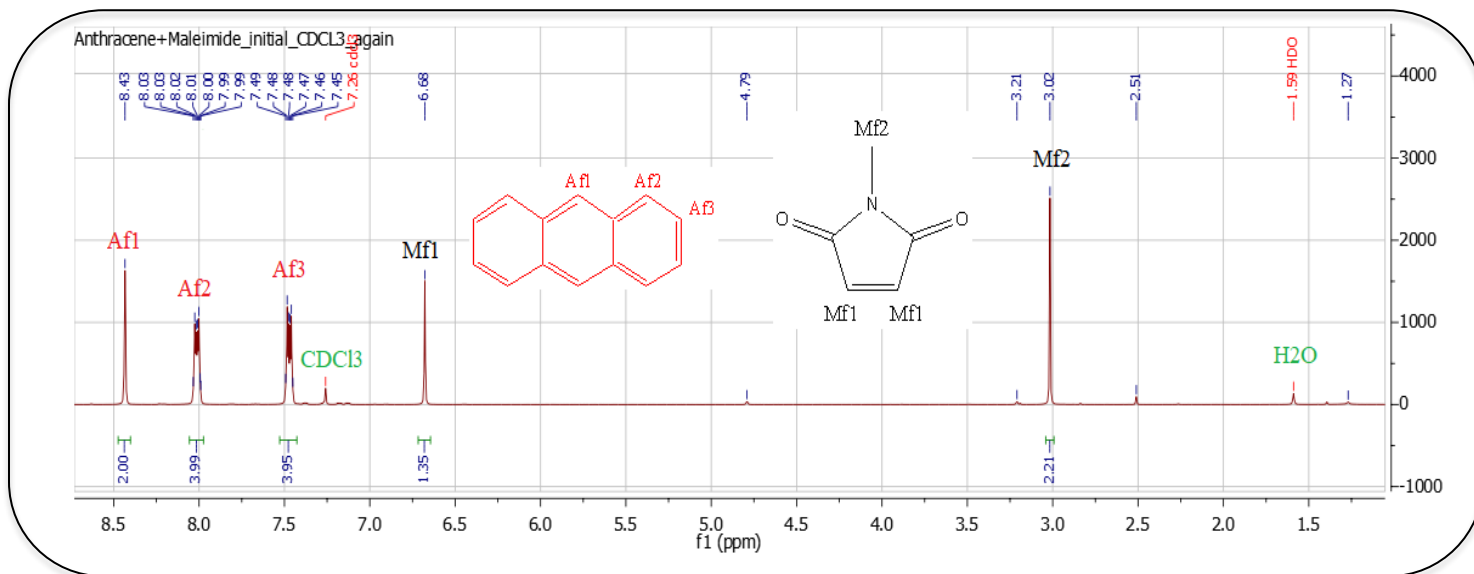


b- ii. 120 °C 24h

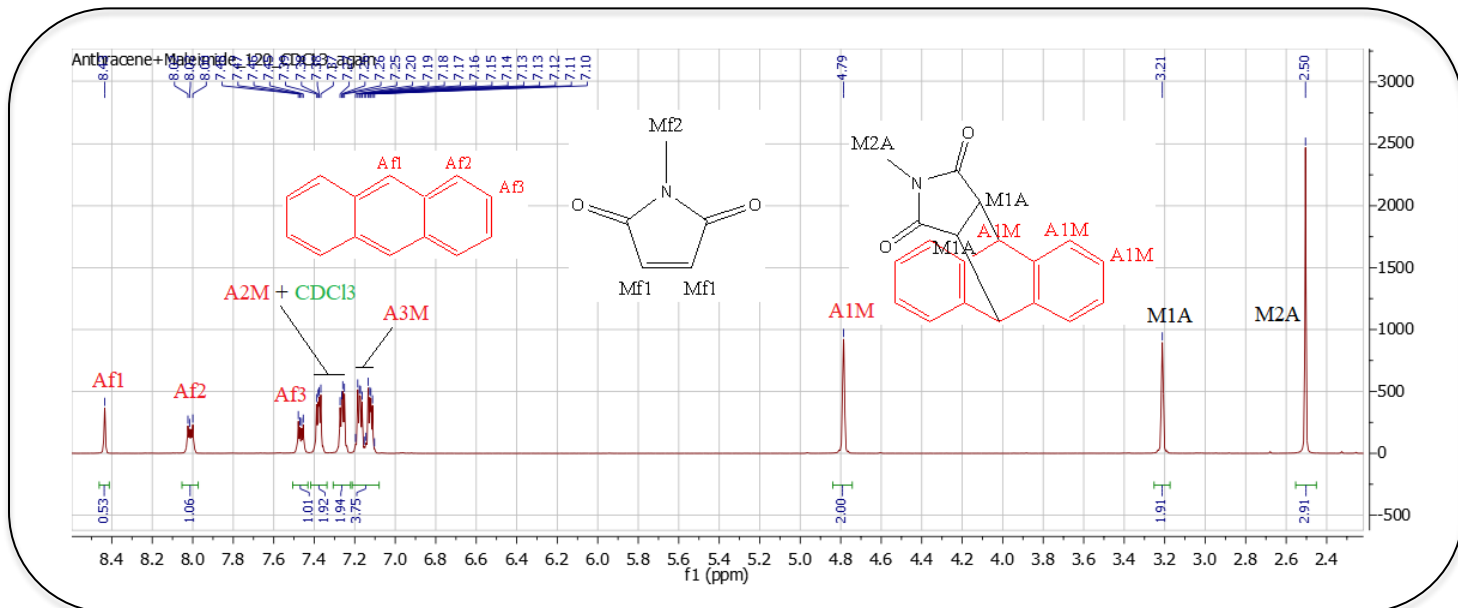


c. An+Ma

c- i. Initial at RT



c - ii. 120 °C 24h



c - iii. UV exposure 5h

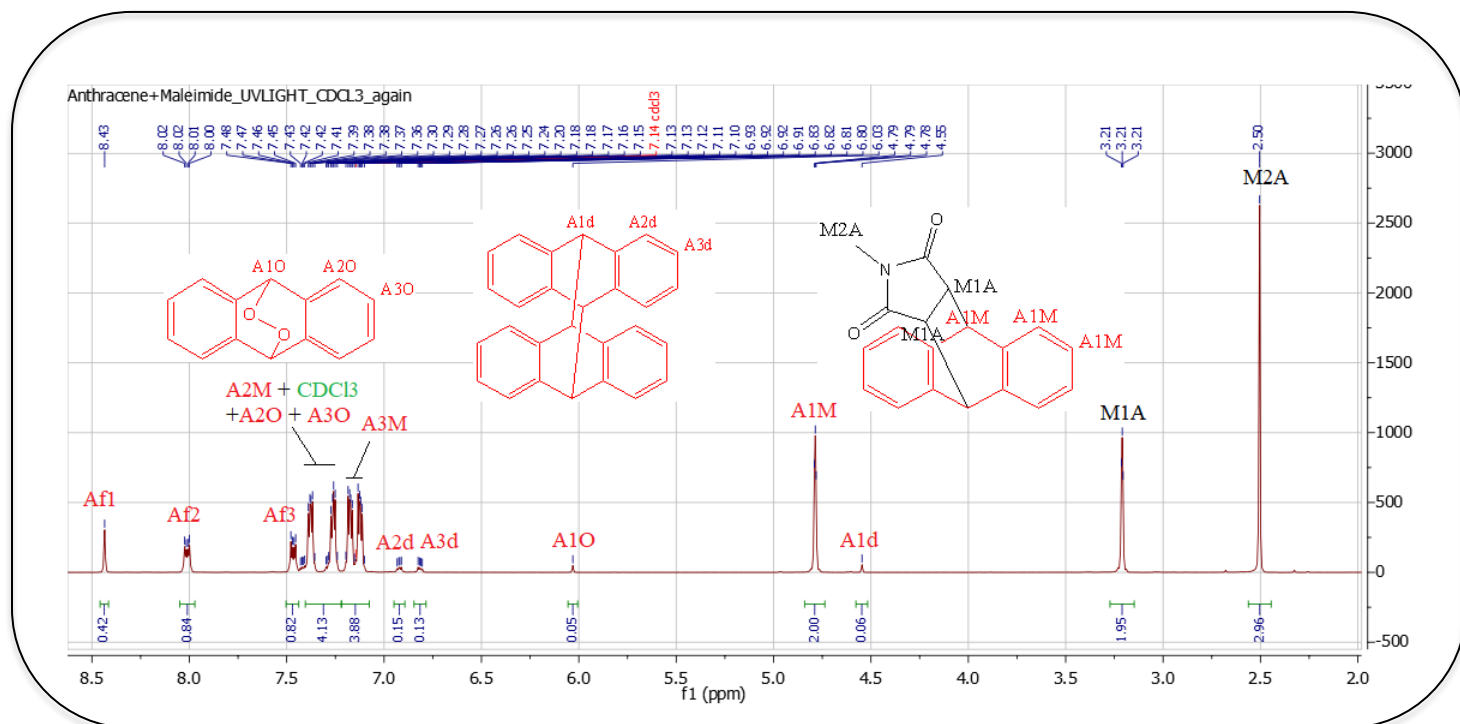


Figure 5 | H-NMR interpretations of reference for reacted model compounds in pairs at different reaction times and temperatures (figure 3b). a) Fu+Ma (i) Initial (ii) 50 °C 24 h The H-NMR spectrum of 50 °C 1h reaction is at Appendix Figure A.1. (iii) 120 °C 30min x and n are referring to exo and endo respectively. b) An+Fu (i) Initial (ii) 120°C 24 h c) An+Ma (i) Initial (ii) 120°C 24h (iii) UV light exposure 5h

Figure 6 shows a dynamics of DA reactions and photodimerization among Fu, Ma and An. It is seen that DA reaction is carried out at low temperature (50°C) between Fu and Ma, and also An and Ma. At high temperature (120°C), It was observed that An replaces Fu to bond with Ma. In addition, photodimerization of An with UV light exposure ($\lambda=365\text{nm}$) was demonstrated. These findings are expected from the literature.

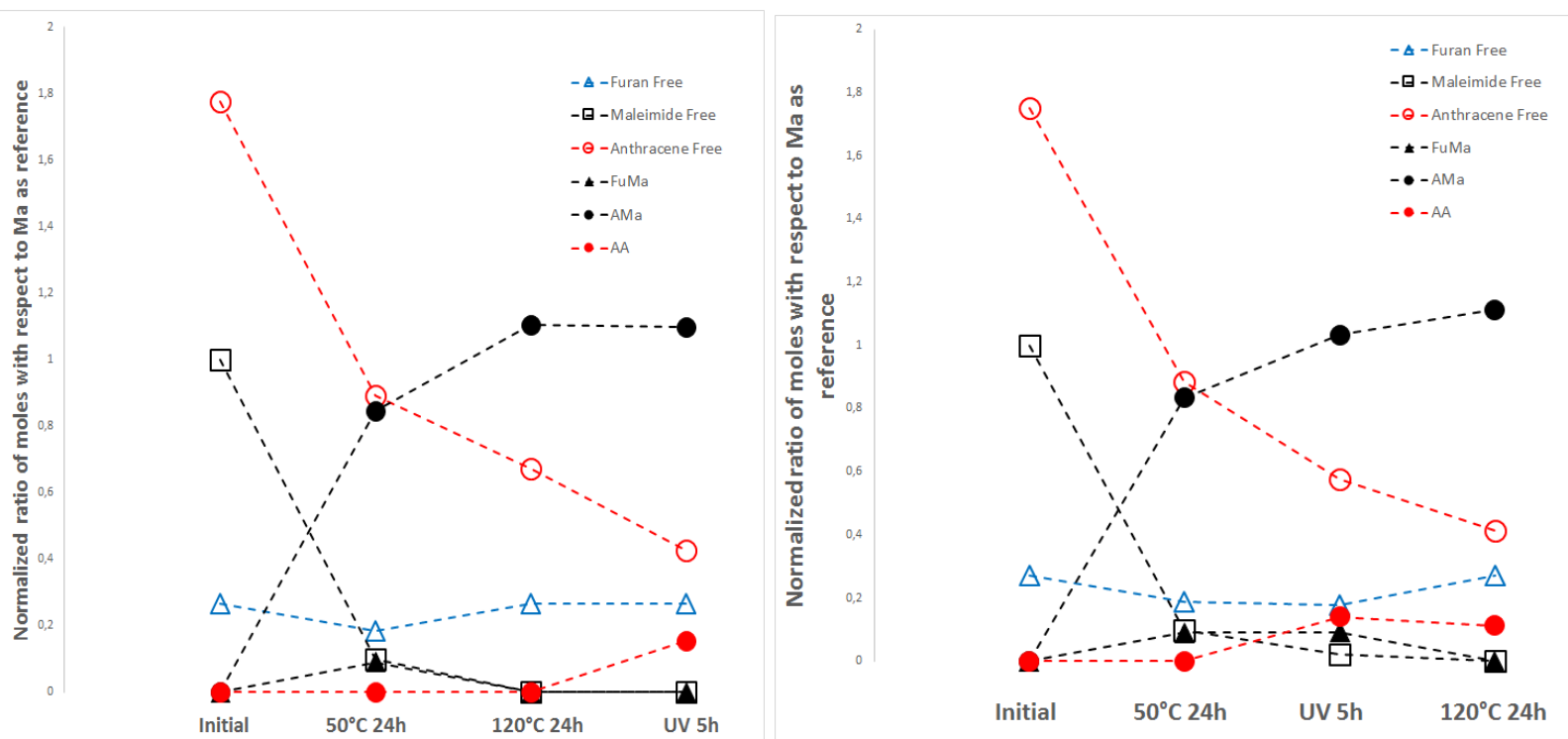


Figure 6 | Reaction of All Model Compounds Together a) Experimental 1 (50°C 24h – 120°C 24h – UV 5h) (left) b) Experimental 2: 50°C 24h – UV 5h – 120°C 24h (right) Empty marks represent the free compounds, and solid marks represent the reacted compounds. Fu free, Ma free and An free are shown triangle blue, square yellow, and circle red respectively. Then reacted compounds are displayed with shape and color where they match with.

The graph indicating the An reactivity at low temperature demonstrates that An is competing with Fu to react with Ma at low temperature. According to the literature [3], a new linkage between An and Ma should be formed while Fu is liberated from Ma at 120°C. However in our case, it was witnessed that both Fu and An are reacting with Ma at low temperature. This can be explained because we worked with small dissolved molecules while literature refers to the polymers. Therefore there might be a mobility or steric issue for them to compete at low temperature. For this reason, we made extra experimentals at lower temperatures of Fu and An with Ma: 30°C and 40°C, to check if we could trigger one of the reactions selectively. The following tables (I,II and III) show the percentage of anthracene free (An), anthracene reacted (An-coupled), maleimide free (Ma), maleimide reacted (Ma-coupled), furan free (Fu), and furan reacted (Fu-coupled) at each temperatures at different reaction time.

30 °C		Conversion percentage through time							
		0h		2h		6h		24h	
		free	coupled	free	coupled	free	coupled	free	coupled
Fu-Ma	Fu	100	-	87.25	12.75	74.44	25.56	40.95	59.05
	Ma	100	-	88.61	11.39	76.46	23.54	45.31	54.69
An-Ma	An	100	-	82.37	17.63	65.3	34.7	29.36	70.64
	Ma	100	-	90.58	9.42	77.34	22.66	53.4	46.6

Table I | AM vs FM percentage of compounds at 30°C

40 °C		Conversion percentage through time							
		0h		2h		6h		24h	
		free	coupled	free	coupled	free	coupled	free	coupled
Fu-Ma	Fu	100	-	70.82	29.18	39.8	60.2	16.09	83.91
	Ma	100	-	75.86	24.14	50.21	49.79	28.1	71.9
An-Ma	An	100	-	76.8	23.2	45.22	54.78	17.76	82.24
	Ma	100	-	85.96	14.03	66.85	33.15	49.74	50.26

Table II | AM vs FM percentage of compounds at 40°C

50 °C		Conversion percentage through time							
		0h		2h		6h		24h	
		free	coupled	free	coupled	free	coupled	free	coupled
Fu-Ma	Fu	100	-	78.49	21.51	43.58	56.42	16.09	83.91
	Ma	100	-	78.49	21.5	43.36	56.37	17.32	82.68
An-Ma	An	100	-	76.05	23.95	41.63	58.37	17.4	82.6
	Ma	100	-	82.9	17.1	58.7	41.3	40.66	59.34

Table III | AM vs FM percentage of compounds at 50°C

It is shown by table I,II and III that the speed of reaction of AM and FM is relatively similar in any low temperatures.

Another remark is the low conversion (~6%) of An dimer under UV light. To examine whether 5 hours of reaction time was not sufficient to satisfy the high efficiency of photodimerization, it was needed to carry out an extra experiment for the An dimerization with 24 hours of reaction time, as shown in Figure 3d. However 24 hours of reaction showed many byproduct peaks besides the An dimer (Figure 7). In other words, 24 hours of reaction time for photodimerization did not produce efficient results as well. According to Breton (1998), this low concentration of photodimerization of anthracene can be explained by the low solubility of anthracene dimer in common organic solvents. It was described by him that with this reason, it is difficult to obtain samples of anthracene dimer in a sufficiently high concentration for H-NMR analysis [15].

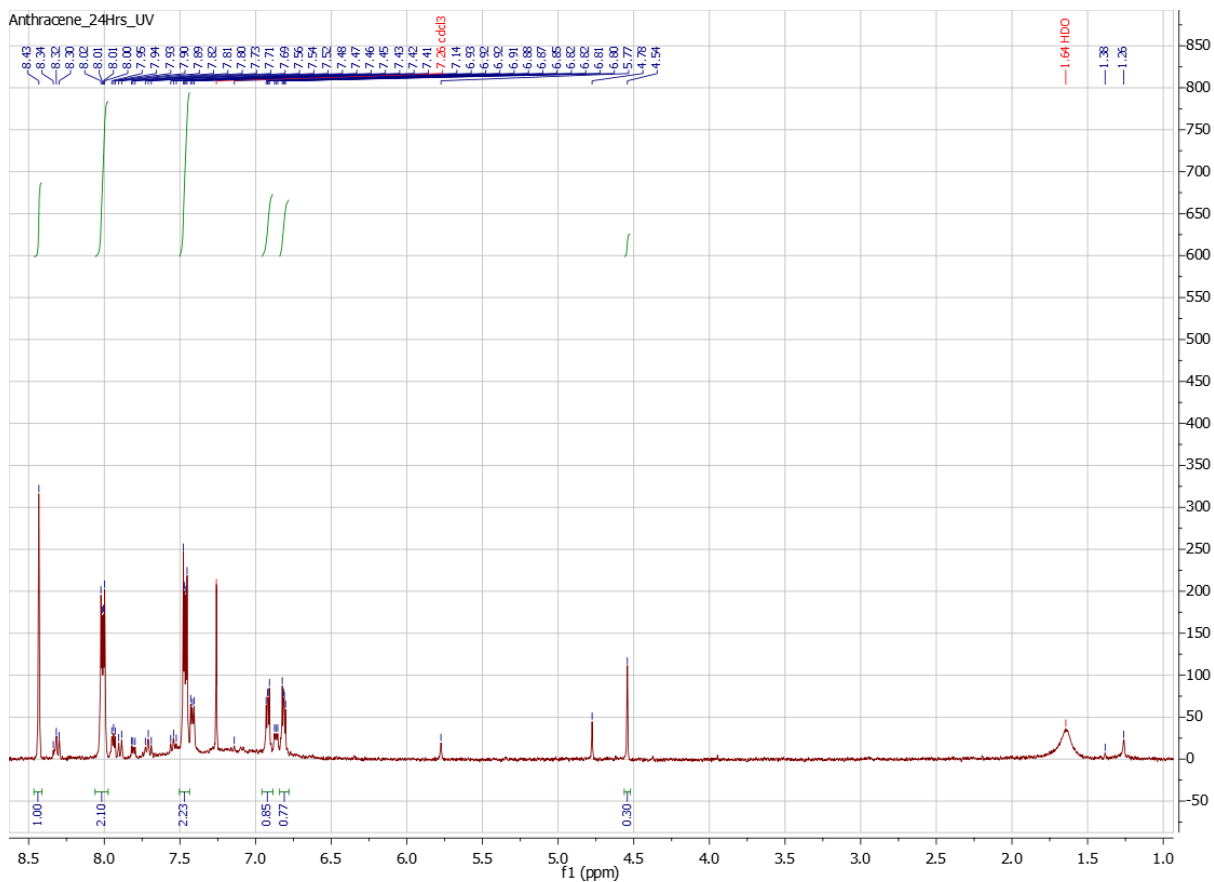


Figure 7 | ¹H-NMR spectrum of An photodimerization after a 24 h reaction.

During this project, to avoid the backfire of radical homopolymerization of maleimide and for better control of our reactions, the system was explored up to 120°C. At 180°C, this system can induce maleimide-maleimide homopolymerization, which was not explored [16]. Additionally, over 120°C in polymer systems, these temperatures might be so high that the polymer could start decomposing.

These precise rules can further influence polymer- research on Fu, Ma and An. These set of reactions based on macromolecular chemistry can be used to prepare for the well-controlled and structured polymers in alternating, block, and graft architecture for the synthesis of new material [17]. This can also lay the groundwork for the promising design of photo-induced self-healing polymers, which is becoming an emerging technology of renewable alternative resources [4][18]. For example, the results allow us to take

an opportunity to apply on a new Fu-Ma crosslinked polymer coating system. The plastic coatings on a product means it is not recyclable. Then we can design coatings on responsive polymers or for treatment of furan-maleimide based coatings. To remove the coatings, anthracene dissolved in solvent can be applied on the coating. By heating it up to 120°C, the coating can be dissolved in the solvent where the Fu can be freed, and Ma can couple with An. This could provide a convenient way for the plastic coatings to be removed, and the product can be recyclable and reusable.

Conclusion

In conclusion, there are three main points that are needed to be highlighted. First, both Fu and An were reacting with Ma at low temperatures (30°C, 40°C, and 50°C). They were competing with each other to react with Ma at a relatively same rate. Second, at 120°C all Fu and Ma bond was broken, and An replaced the Fu, reacting with Ma. Reversibly disassociation between Fu and Ma was carried out, which gave free Ma to react with An even more at higher temperature. Lastly, it showed low concentration of An photodimerization through UV light ($\lambda=365\text{nm}$). Although the wavelength of UV light was in the range of photodimerization wavelength ($\lambda>300\text{nm}$), low concentration of the An dimers was demonstrated due to the organic solvent we used. This work set the basics through models in order to design responsive polymers on the basis of these reactions. This study on dynamics of DA reaction and photodimerization will help to develop responsive polymer systems based on Fu, Ma and An chemistries.

Reference

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Appendix

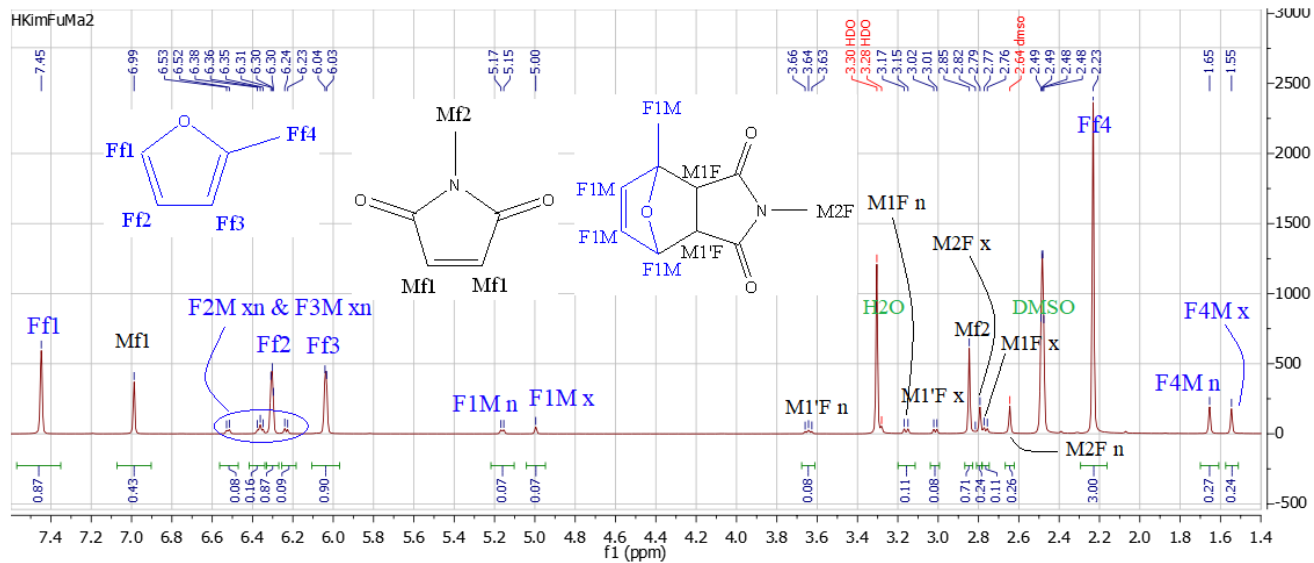


Figure A.1 | H-NMR interpretation of Fu+Ma at 50 °C 1h reaction