Electronic Supplementary Material (ESI) for ChemComm.

Fe_3O_4 Nanoparticles as Robust Photothermal Agents for Driving High Barrier Reactions under Ambient Conditions

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Supporting Information

Experimental Details

Synthesis of magnetic iron oxide nanoparticles

$Fe(acac)_3$ (2 mmol), oleylamine (7 mmol), oleic acid (6 mmol), tetradecanediol (10 mmol), and diphenyl ether (20 mL) were combined and stirred while purging with nitrogen gas for 30 minutes. Under a nitrogen atmosphere, the solution was brought up to 200 °C for 2 hours and then brought to reflux (~300 °C) for 1 hour. The solution was allowed to cool to room temperature and the MNPs were precipitated with acetone, magnetically collected, and the yellow supernatant decanted. The MNPs were then washed with acetone until the supernatant became clear and allowed to dry. Figure S1 shows the UV-Vis spectrum of the resulting MNPs in hexanes.

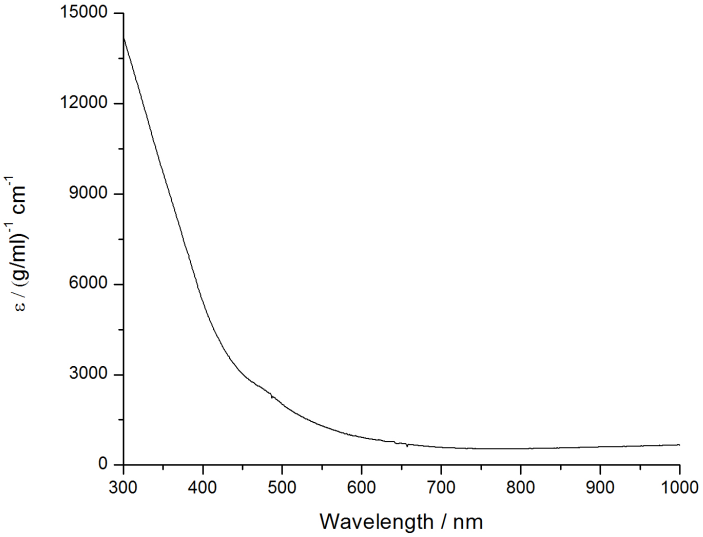

Figure S1. UV-Vis spectrum of as synthesized magnetite nanoparticles

Preparation of MNP:PPC films

Polypropylene carbonate was dissolved in dichloromethane (DCM) such that the concentration of 0.2 g PPC/mL DCM was achieved. MNPs were then dissolved in as little hexane as possible and slowly added to the PPC solution drop-wise, while stirring, until the desired mass percentage of MNP was obtained. The MNP:PPC solution was then drop cast onto a pre-weighed slide with a diameter similar to that of the lasers beam (~ 8 mm). The slides were then dried overnight before being irradiated. Before irradiating each slide, the energy of the beam was measured with an ES220C power meter (Thorlabs) to ensure consistent conditions.

Estimation of the lower temperature limit

The lower temperature limit was calculated by assuming that the heat generated by the MNPs is fully delocalized, giving a uniform temperature within the film during irradiation. For this, the 1:100 sample was used which displayed ~36% decomposition after 56 μs irradiation time, which corresponds to 0.7 half-lives. Assuming first order reaction kinetics, the rate can be calculated by:

$$t_{1/2} = 0.693 * k \tag{1}$$

where $t_{1/2}$ is the half-life and k is the rate. This gives a rate of 8660 s^{-1}. The temperature required for this rate to be observed can be found using the Arrhenius equation:

$$k = Ae^{\frac{-\Delta G^{\ddagger}}{RT}} \tag{2}$$

where $\Delta G^{\ddagger}$ is the activation energy, R is the gas constant, and T is the temperature. It is also assumed that the pre-exponential factor is dominated by the bond that is broken (C-O) which is 2.4 x 10^{-12} s^{-1}. This gives us the minimum temperature the film would have to reach for the reaction to proceed at the observed rate, which is 770 K.

Stability of MNPs during irradiation in polypropylene carbonate films

Shown in Figure S2 are TEM images of MNPs before irradiation and after irradiation in the polymer sample. Although some growth is apparent, only a small fraction of the MNPs exhibit growth. This is contrary to the stability of AuNPs which were shown to grow ~1000% in diameter. This supports the increased stability of MNPs over that of AuNPs. For reference, gold nanoparticles are shown before and after irradiation in PPC films (S3), as well as hexane solutions (S4).

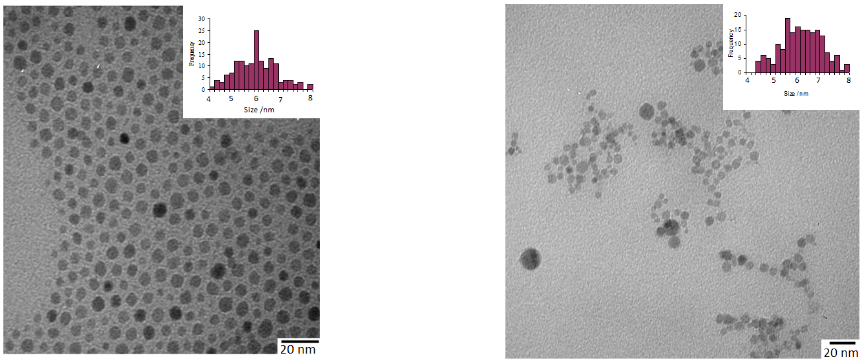

Figure S2. TEM images of MNPs before (left) and after (right) irradiation in MNP:PPC films

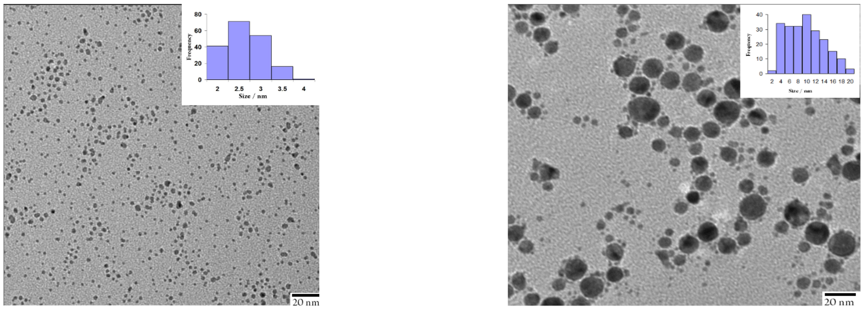

Figure S3. TEM images of gold nanoparticles before (left) and after (right) irradiation in AuNP:PPC films

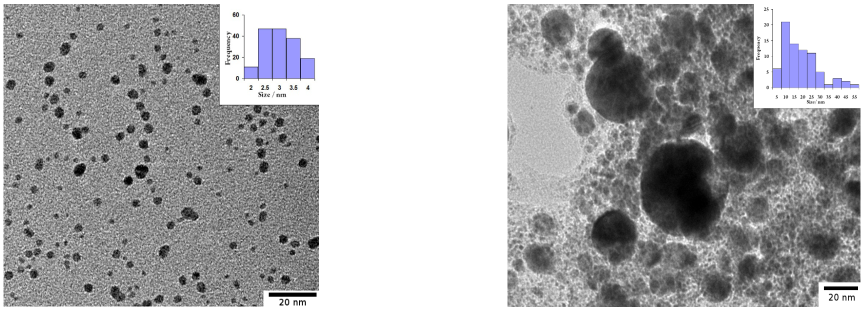

Figure S4. TEM images of gold nanoparticles before (left) and after (right) irradiation in hexane solution.

Characterization of gaseous products

Irradiation of the PPC film yielded gaseous products, which were characterized using ^{1}H NMR. This gas was condensed in a receiving vial that was immersed in a liquid nitrogen bath. The use of the receiving vial assured that no polymer would contaminate the desired sample, as well as allowed for the maximum amount of products to be collected to optimize the NMR signal. The NMR spectra for both the polymer and the condensed products are shown Figure 1 of the manuscript.

To further elucidate the identity of the products formed during irradiation, the gaseous products were analyzed by mass spectrometry. This was done by casting a composite film in a Schlenk flask which was then put under vacuum and irradiated. The gaseous products that remained in the headspace of the flask were then injected into the spectrometer. Neat monomer was also analyzed by the same instrument with the injection port set at 200°C for comparison. As shown in Figure S5, the products collected show the same major peaks as the pure monomer. The lack of the minor peaks in Figure S3a is attributed to the fact that propylene carbonate has a low vapor pressure at room temperature and thus little monomer is left in the headspace of the flask. However, we emphasize that the results are consistent with the presence of volatile propylene carbonate in the headspace of the reaction vial – as predicted by the thermal degradation pathways of PPC.

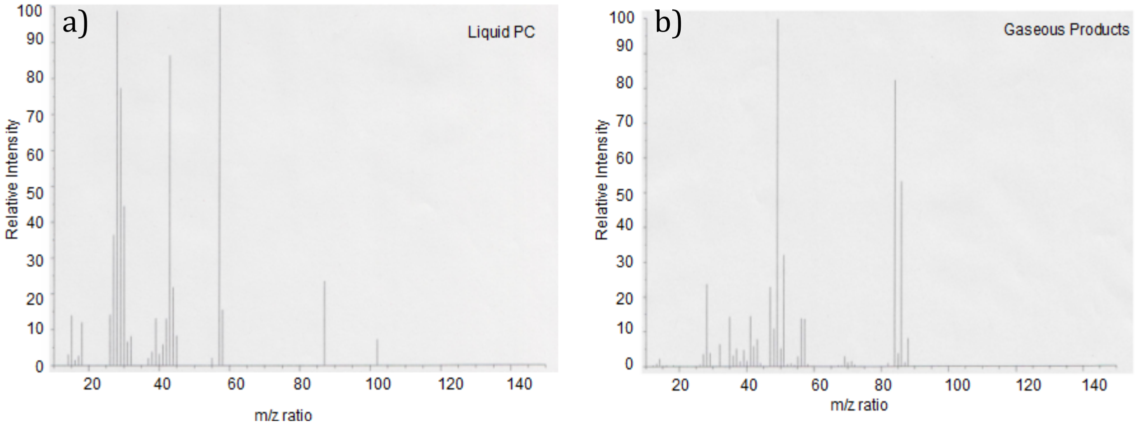

Figure S5. Mass spectra of (a) pure propylene carbonate (b) the headspace collected above a PPC/MNP film after irradiation.

Control experiments:

To ensure that the MNPs were solely responsible for the degradation observed in the PPC films, as well as the ligands were not undergoing any unexpected changes, control experiments were carried out. Firstly, irradiation of PPC films without MNPs present were irradiated with a power of 50 MW cm^{-2} to observe any mass loss not attributed to the heat generated by the MNPs. Secondly, IR and NMR spectroscopies were employed to ensure that oleylamine was not effected by the intense radiation. Figure S6 shows IR and ^{1}H NMR spectra of oleylamine before and after being irradiated with a power of 50 MW cm^{-1}. Both sets of spectra show that oleylamine is indeed unchanged after irradiation.

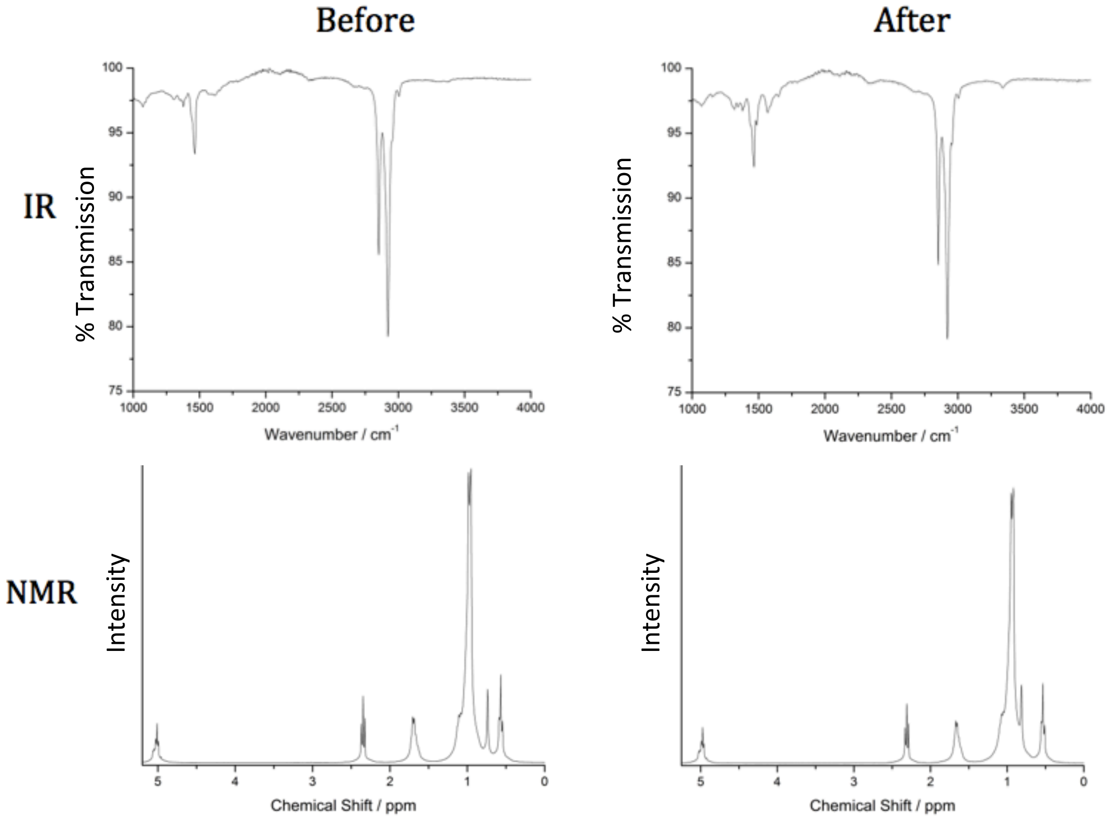

Figure S6. IR (top) and NMR (bottom) of oleylamine before (left), and after (right) irradiation at 50 MW cm^{-1}