Electronic Supplementary Information

Repairable photoactive polymer systems via metal-terpyridine-based self-assembly

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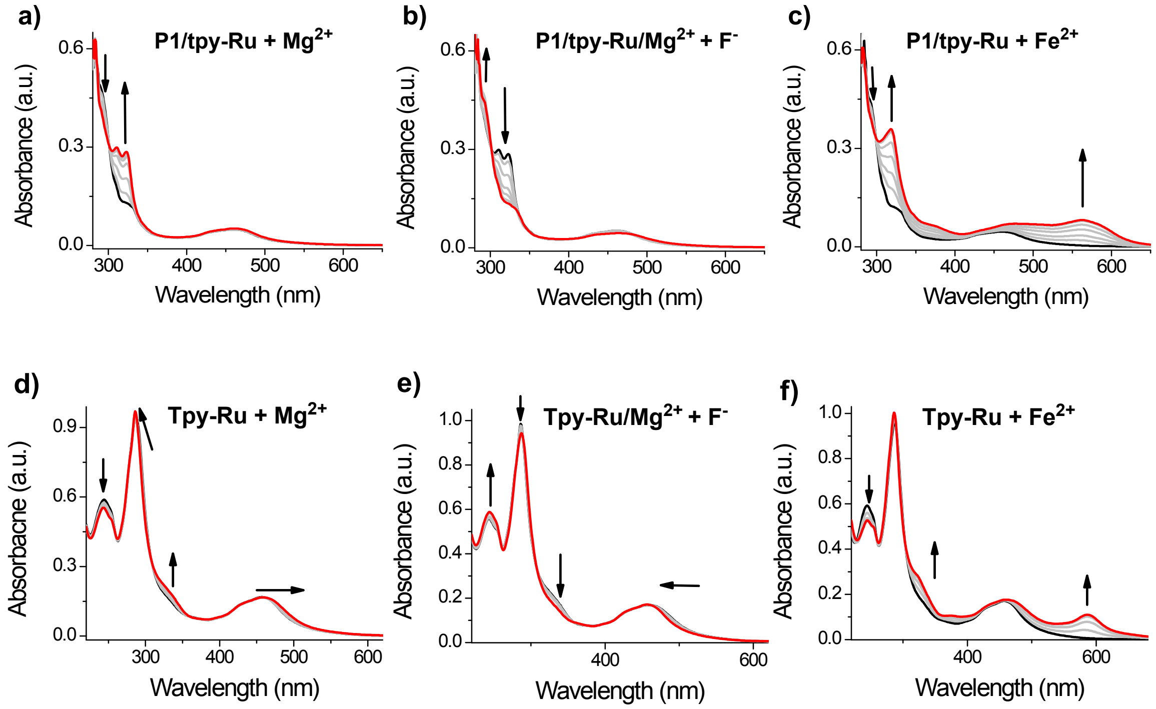

Figure S1. (a-c) UV-vis absorption spectra of tpy-polymer P1 (0.1 mg) and tpy-Ru (0.01 mg) in THF (3 mL) with addition of Mg^{2+} (a) or Fe^{2+} (c) (1 mM, 5-μL intervals) (assembly), and subsequent addition of TBAF (10 mM, 1-μL intervals) in a (b, disassembly). (d-f) UV-vis absorption spectra of tpy-Ru (10 μM) in THF with addition of Mg^{2+} (d) or Fe^{2+} (f) (1 mM, 5-μL intervals) (assembly), and subsequent addition of TBAF (10 mM, 1-μL intervals) in d (e, disassembly).

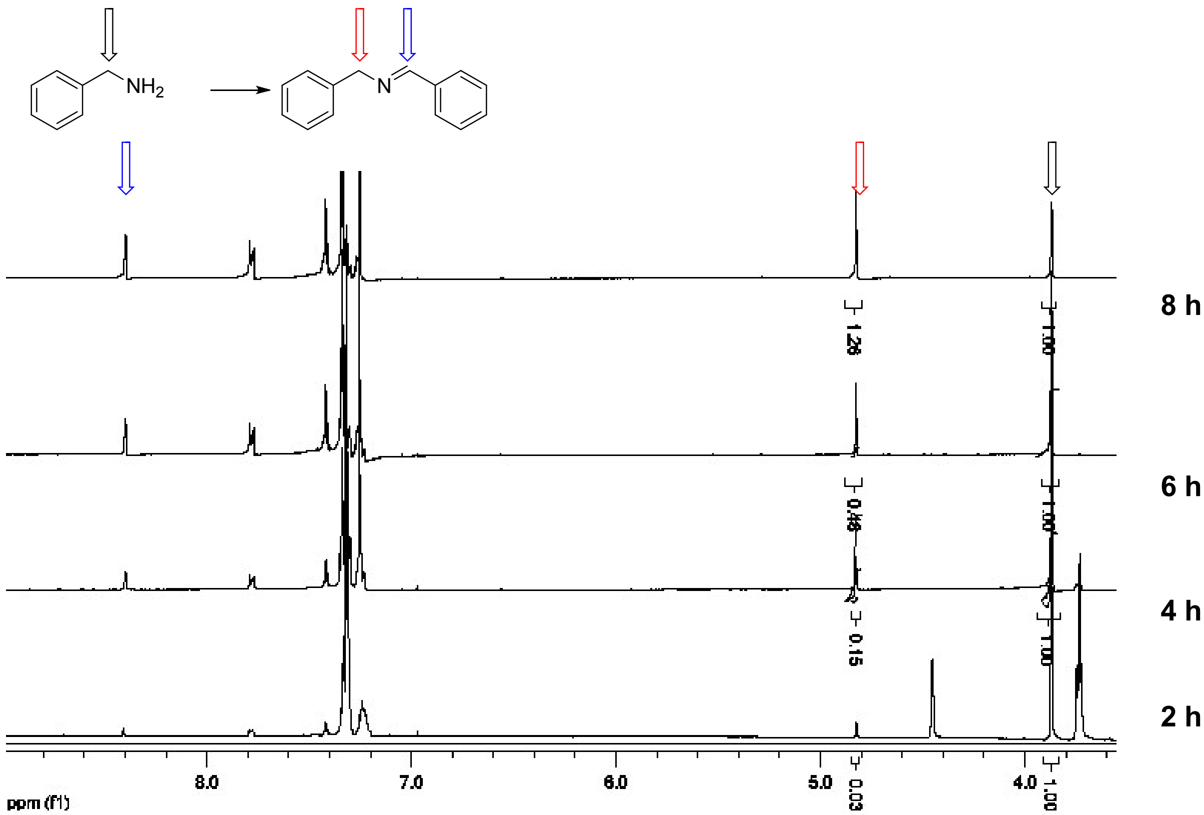

Figure S2. [1]H-NMR spectra with time in P1/tpy-Ru with Mg^{2+} showing the photocatalytic conversion of benzylamine to benzylbenzaldimine.

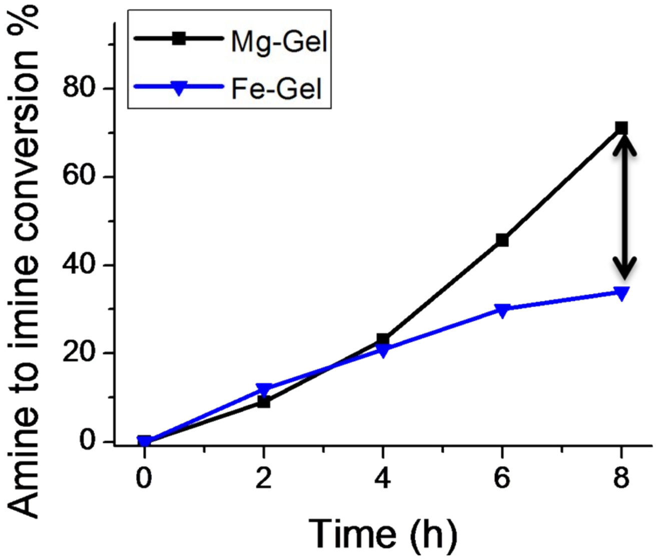

Figure S3. Comparison of conversion rates in photocatalytic oxidation of amine to imine with self-assembled gels P1/tpy-Ru with Mg^{2+} and Fe^{2+}.

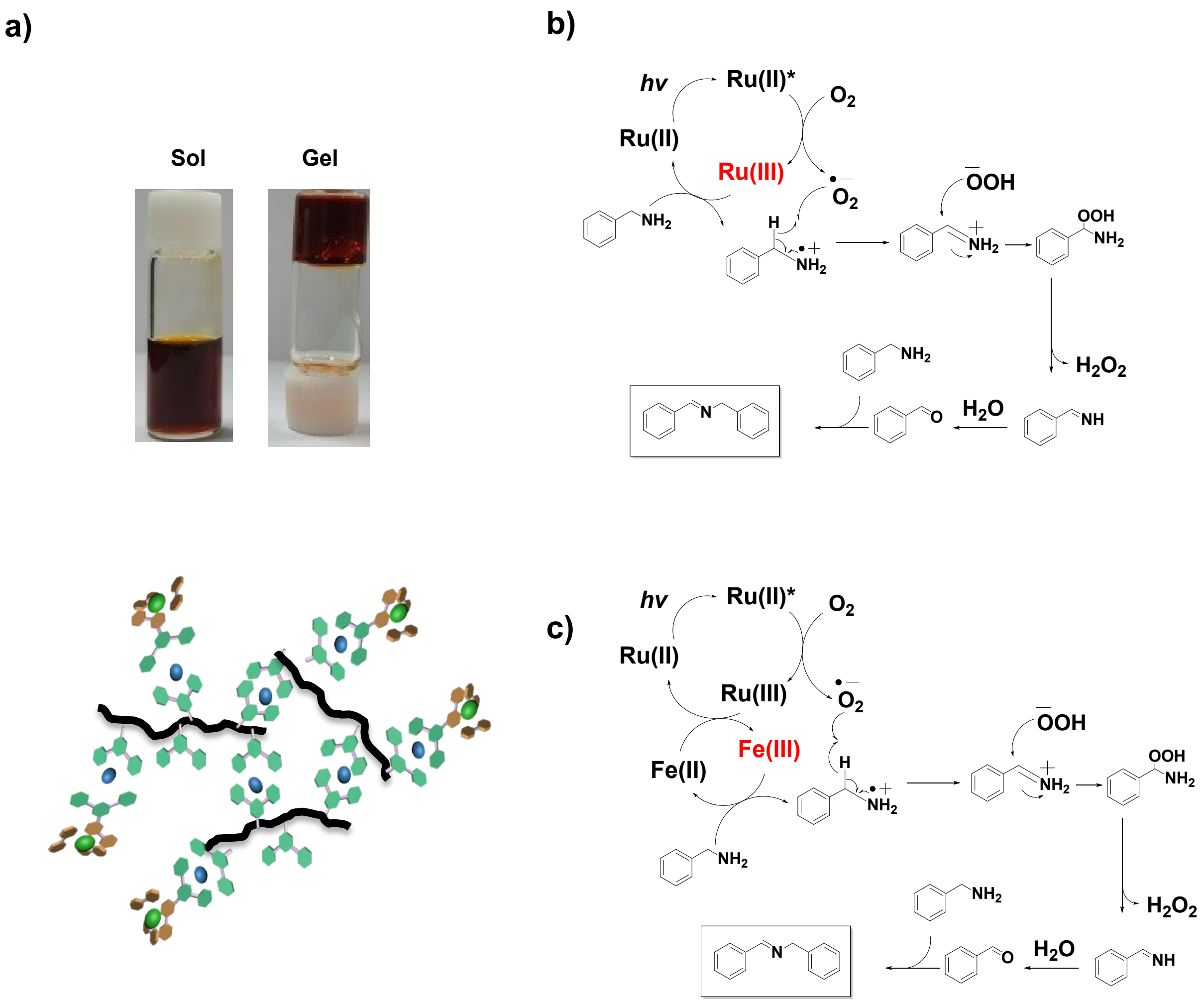

Figure S4. (a) Sol-gel phase change of P1 with Mg^{2+}. (b, c) Proposed mechanisms of photoinduced oxidation of benzylamine to benzylbenzaldimine in tpy-Ru/Mg(II) complex (b) and in tpy-Ru/Fe(II) complex (c).

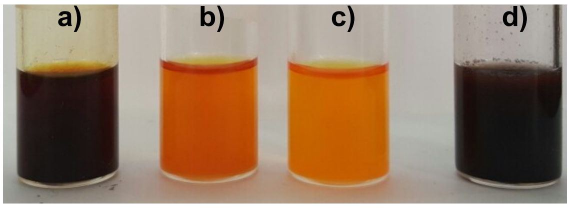

Figure S5. (a) Image of a redox titration using a KI/starch solution, which consists of starch (5 mg), 0.1 M KI, and 0.1 M acetic acid, for generation of hydrogen peroxide in photoinduced oxidative coupling of benzylamine (122 mM) to benzylbenzaldimine with $Ru(bpy)_3{\cdot}2PF_6$ (1 mol%) in 3 mL THF/H_2O (2:1) after irradiation for 12 h using a 455-nm LED lamp under air atmosphere. (b) Negative control without benzylamine. (c) Negative control without 455-nm irradiation. (d) Direct addtion of H_2O_2 (35%, 40 μL) to the KI/starch solution.

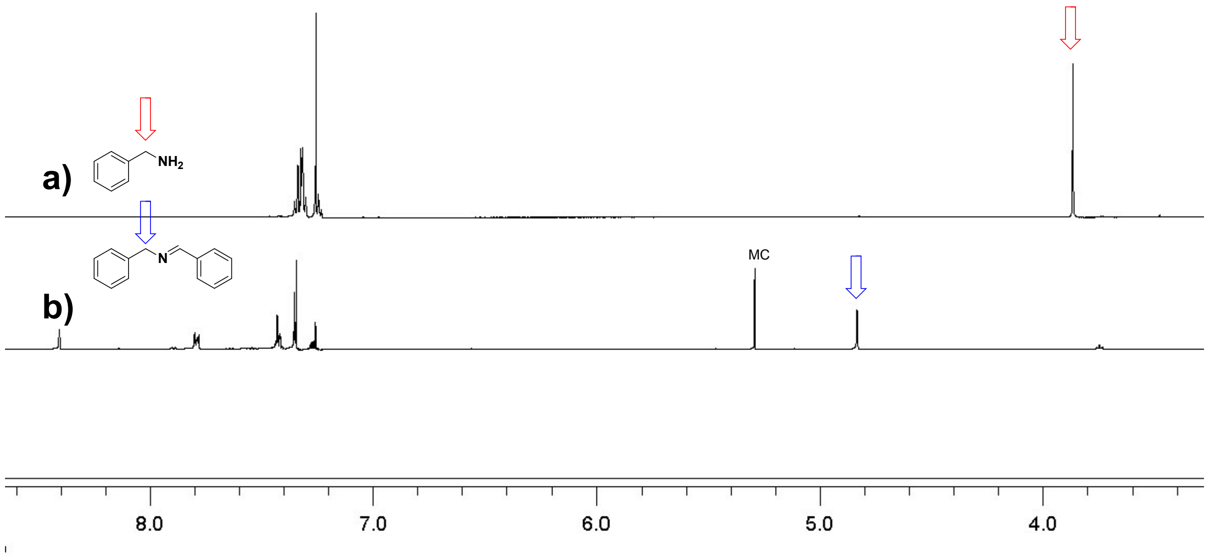

Figure S6. Comparison of ^{1}H-NMR spectra to confirm the generation of superoxide ($O_2^{\cdot -}$) in photoinduced oxidative coupling of benzylamine to benzylbenzaldimine. (a) In the presence of superoxide dismutase (SOD, $O_2^{\cdot -}$ scavenger) in the photocatalytic reaction mixture, the yield was less than 1% using benzylamine (122 mM) and $Ru(bpy)_3{\cdot}2PF_6$ (1 mol%) in 3 mL THF/H_2O (2:1) after irradiation for 12 h using a 455-nm LED lamp under air atmosphere. (b) Without SOD, the yield was ~99% under similar conditions.

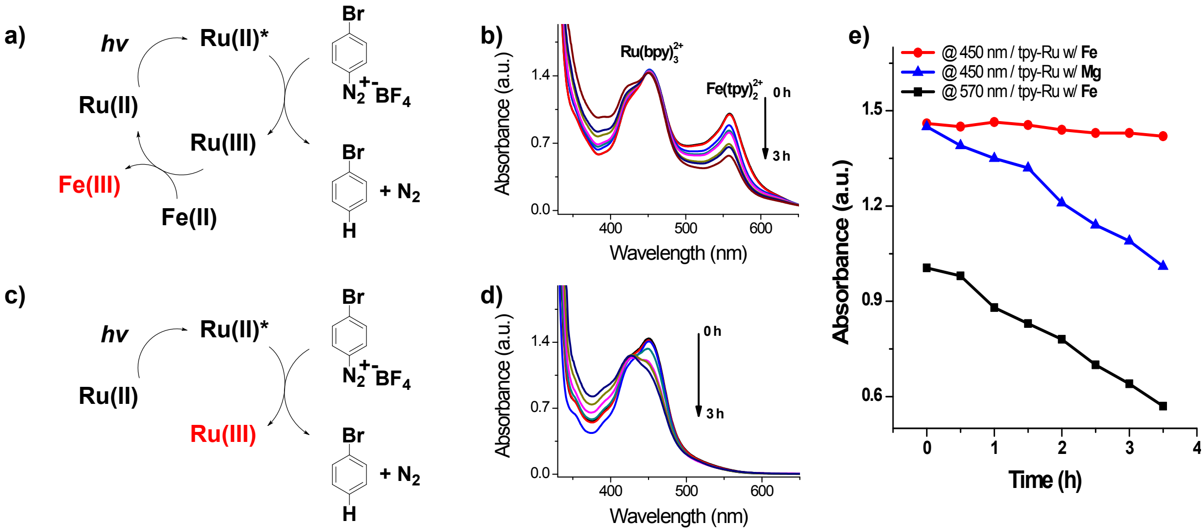

Figure S7. Comparisons of photoinduced electron transfer mechanism between a tpy-Ru/Fe(II) complex (a) and a tpy-Ru/Mg(II) complex (c) in the presence of an irreversible electron acceptor, 4-bromophenyl diazonium salt. Changes of UV-vis absorption spectra during the irradiation using assembled tpy-Ru/Fe(II) (b) and tpy-Ru/Mg(II) (d), and time-elapsed absorbance changes (e).

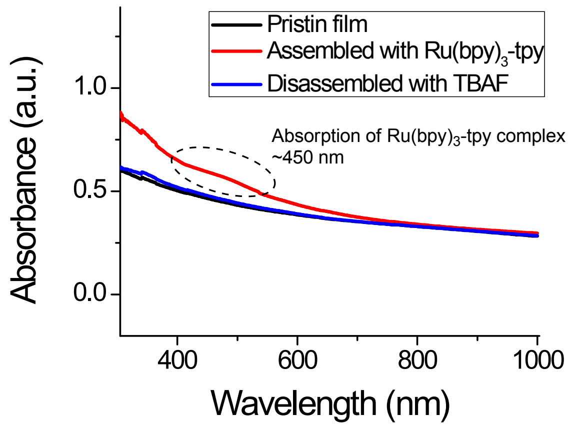

Figure S8. UV-vis absorption spectra of tpy-functionalized polymer P1 and tpy-MWNT hybrid film (black line), tpy-Ru assembled hybrid film with Mg^{2+} (red line), and disassembled hybrid film using TBAF (blue line).

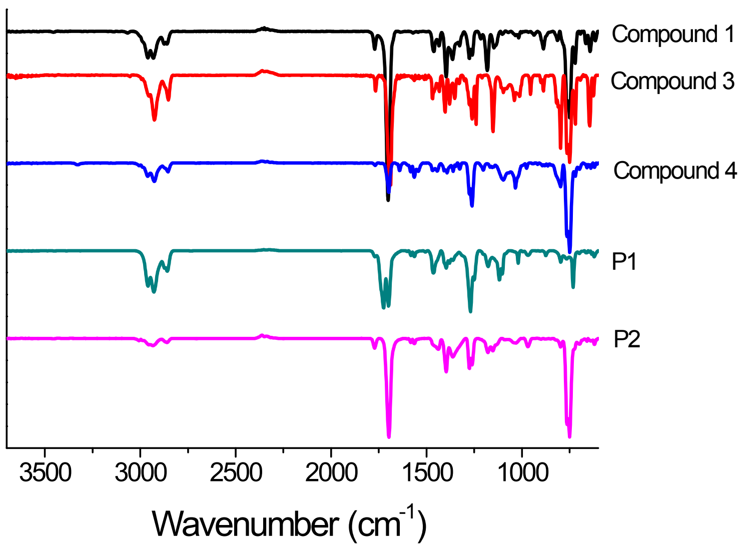

Figure S9. FT-IR spectra of norbornene derivatives, compounds 1, 3, 4, P1 and P2.

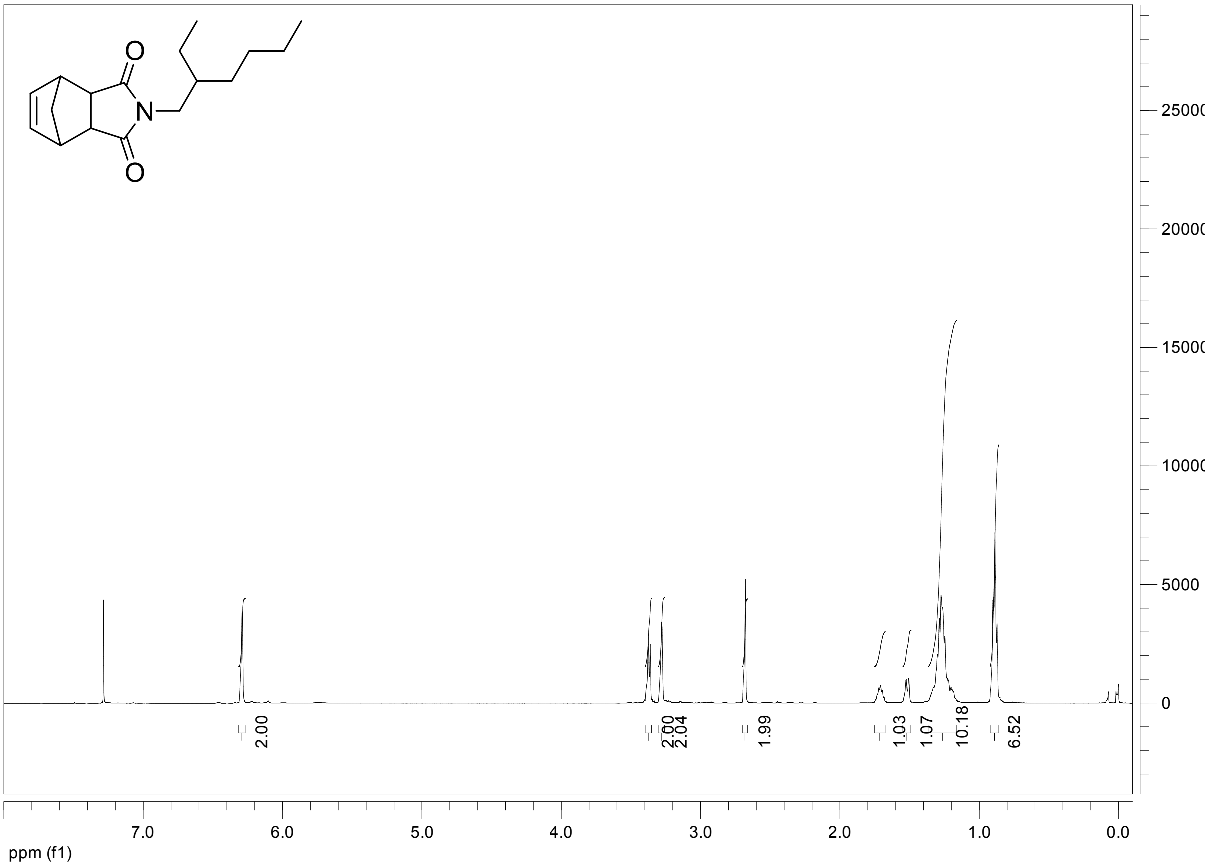

Figure S10. ^{1}H-NMR spectrum of compound **1.**

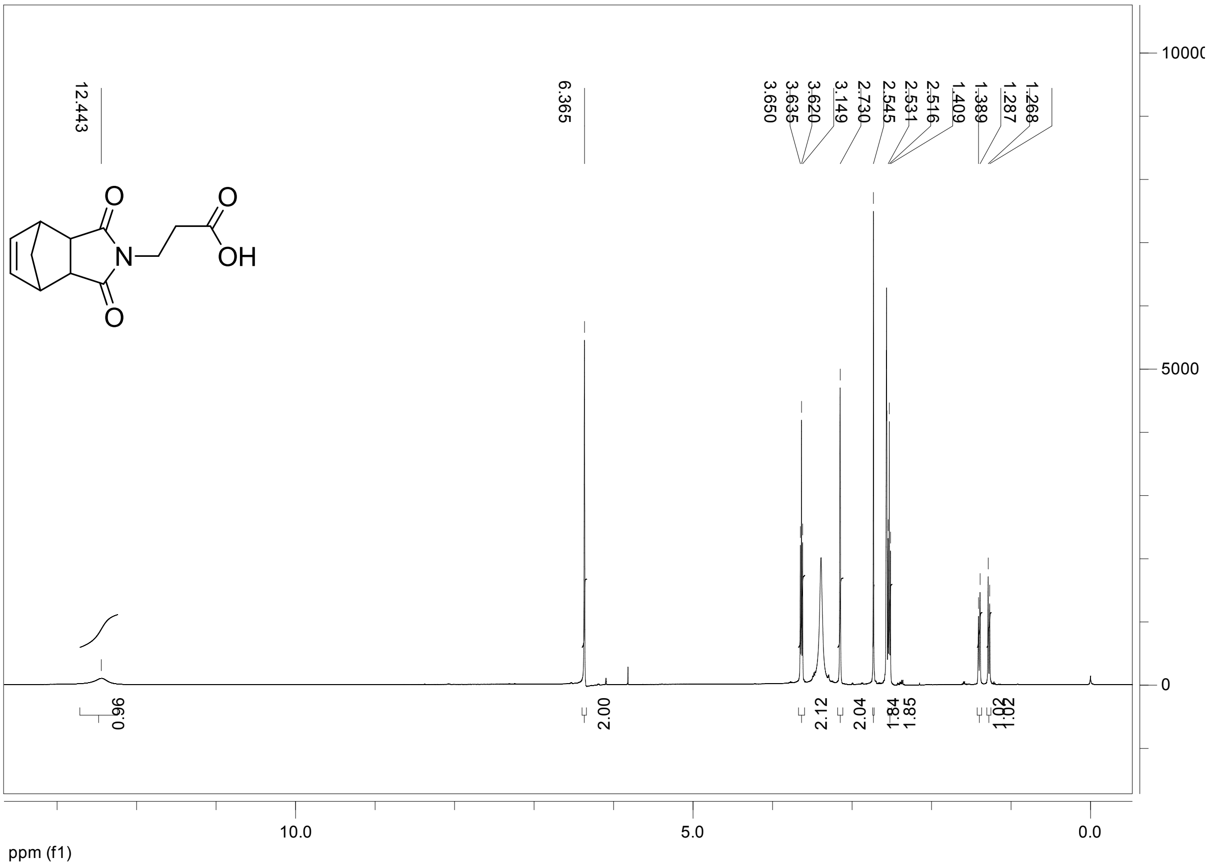

Figure S11. [1]H-NMR spectrum of compound **2.**

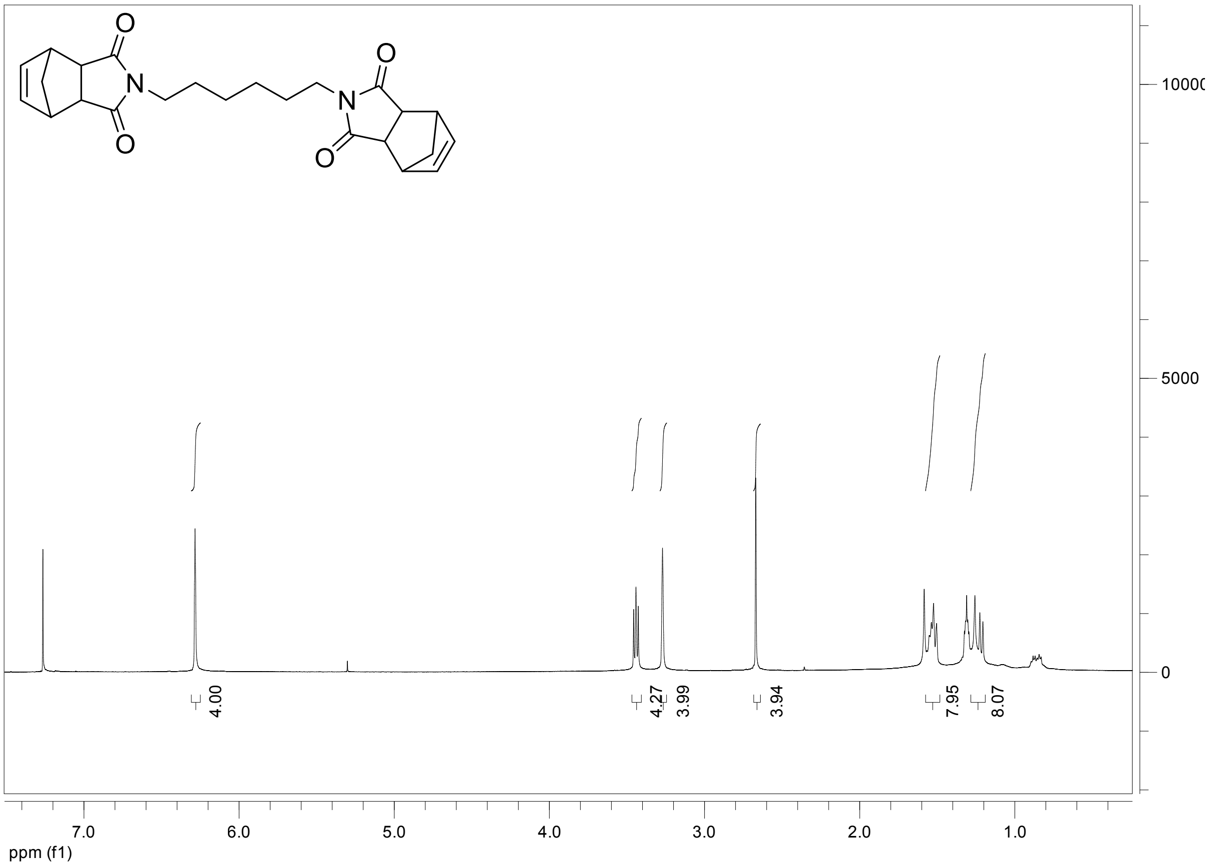

Figure S12. ^{1}H-NMR spectrum of compound **3.**

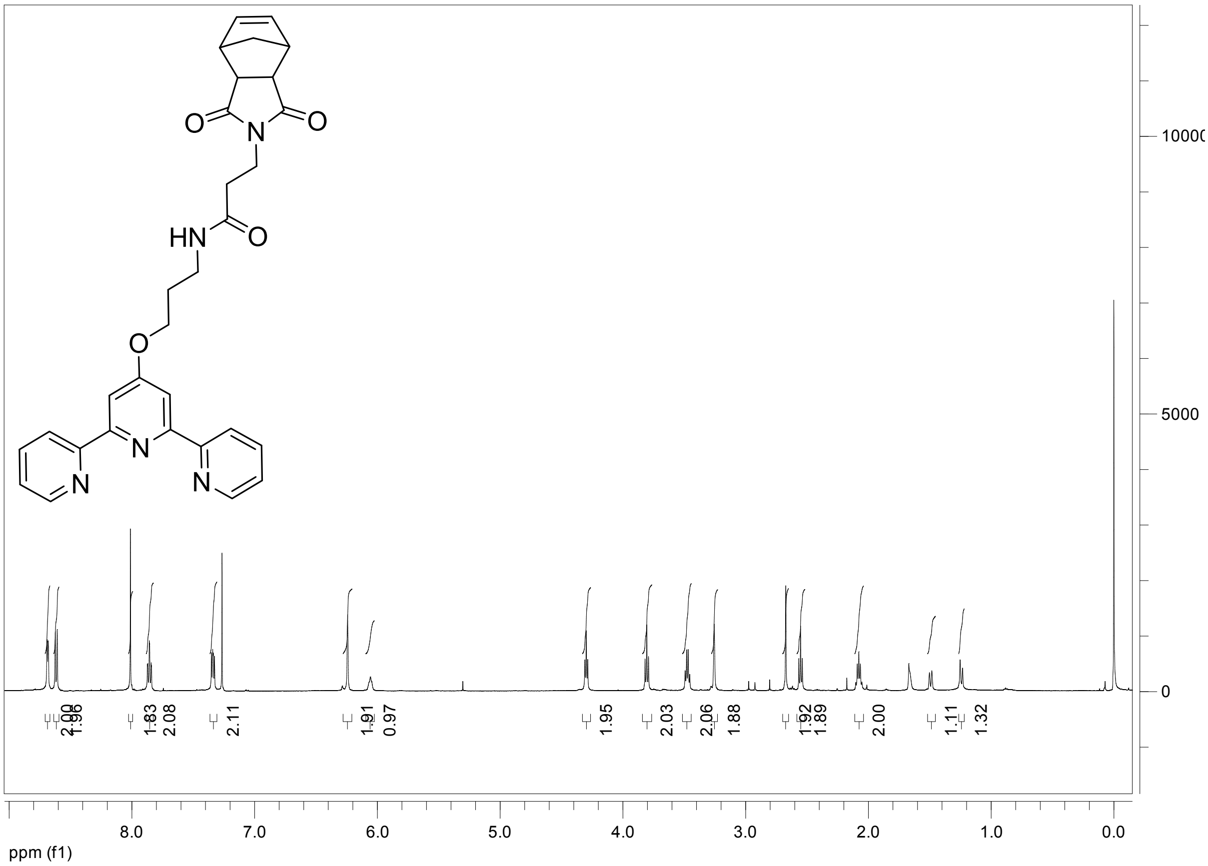

Figure S13. ^{1}H-NMR spectrum of compound **4.**

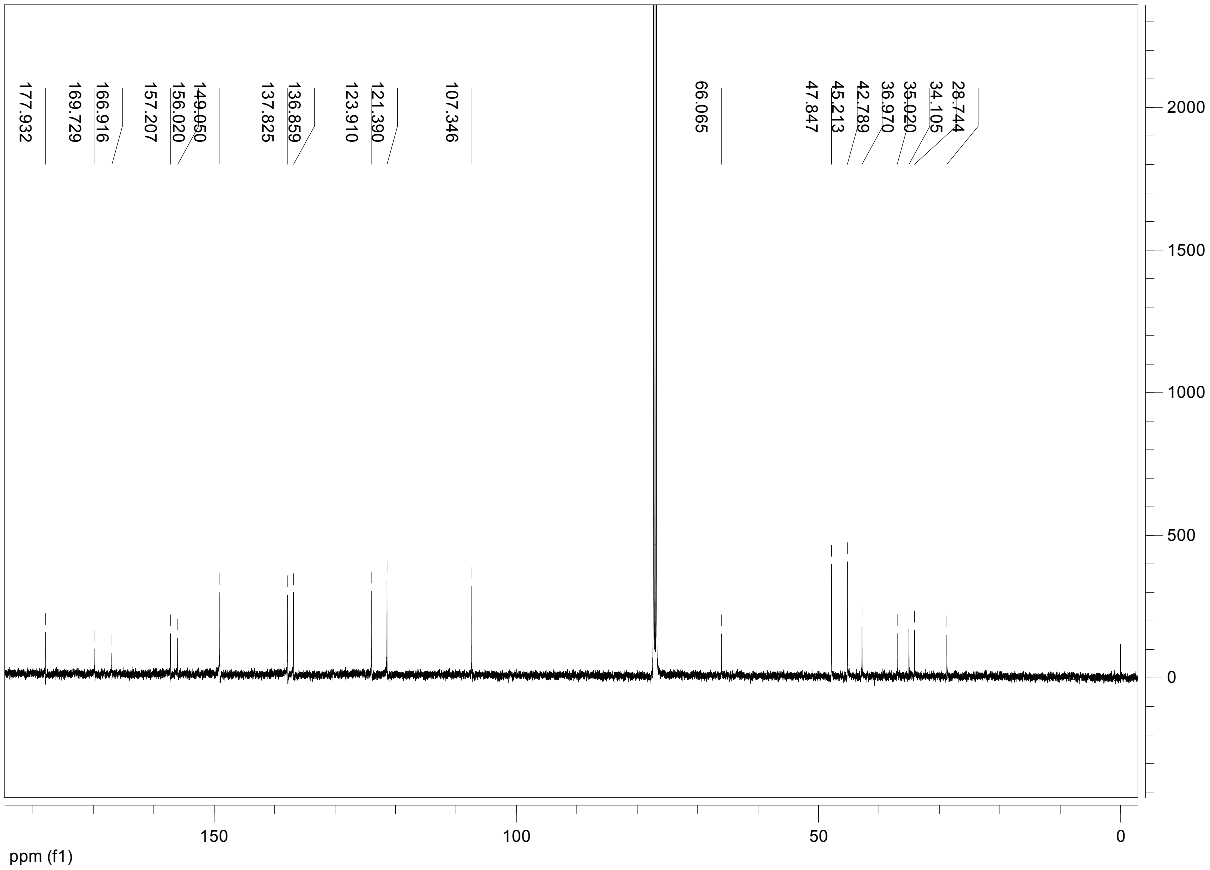

Figure S14. ^{13}C-NMR spectrum of compound **4.**

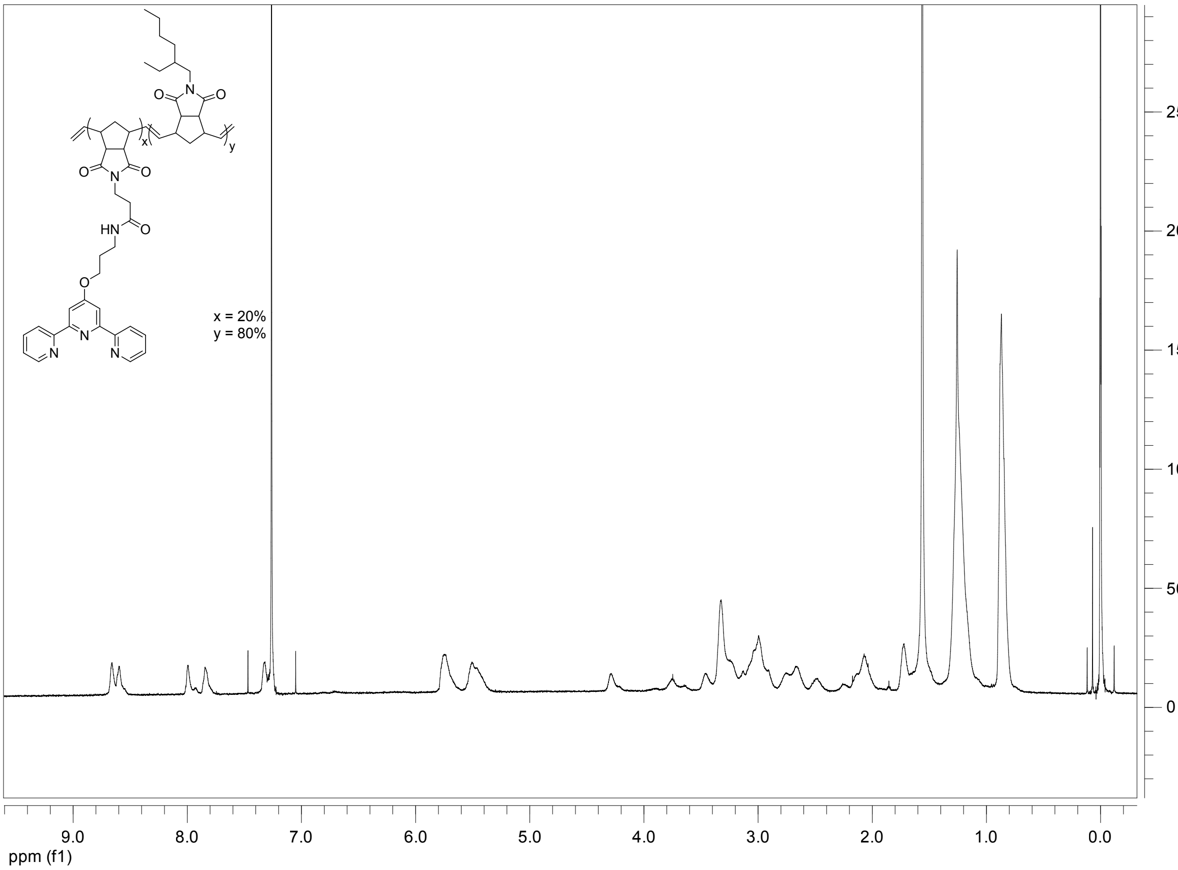

Figure S15. ^{1}H-NMR spectrum of P**1.**