Electronic Supplementary Information

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

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✓ Figure S1. Absorption of tpy-polymer and Ru(bpy)$_2$bpyp-tpy
✓ Figure S2. Conversion calculation of benzylimin using $^1$H-NMR spectra with time in Mg-gel and assign of benzylimine from produced photocatalysis.
✓ Figure S3. Comparison of photocatalytic amine to imine conversion with self-assembled gel by Mg$^{2+}$ and Fe$^{2+}$.
✓ Figure S4. Proposed mechanisms of photoinduced oxidation of benzylamine to benzylbenzaldimine.
✓ Figure S5. Image of a redox titration using a KI/starch solution.
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✓ Figure S7. Comparison mechanism of electron transfer between Fe-tpy$_2$ complex and Mg-tpy$_2$ complex.
✓ Figure S8. UV-vis absorption of tpy functionalized polymer and MWNTs hybrid films.
✓ Figure S9. FT-IR spectra of norbornene derivative (compound 1,3 and 4), P1 and P2.
✓ Figure S10~13. $^1$H-NMR spectrum of compound 1~4 and P1.
✓ Figure S14. $^{13}$C-NMR spectrum of compound 4.
✓ Figure S15. $^1$H-NMR spectrum of P1.
**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 benzylbenzaldehyde.
**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$2PF$_6$ (1 mol%) in 3 mL THF/H$_2$O (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 addition of H$_2$O$_2$ (35%, 40 μL) to the KI/starch solution.
Figure S6. Comparison of $^1$H-NMR spectra to confirm the generation of superoxide ($O_2^-$) in photoinduced oxidative coupling of benzylamine to benzylbenzaldimine. (a) In the presence of superoxide dismutase (SOD, $O_2^-$ scavenger) in the photocatalytic reaction mixture, the yield was less than 1% using benzylamine (122 mM) and Ru(bpy)$_3$-2PF$_6$ (1 mol%) in 3 mL THF/H$_2$O (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 P1.