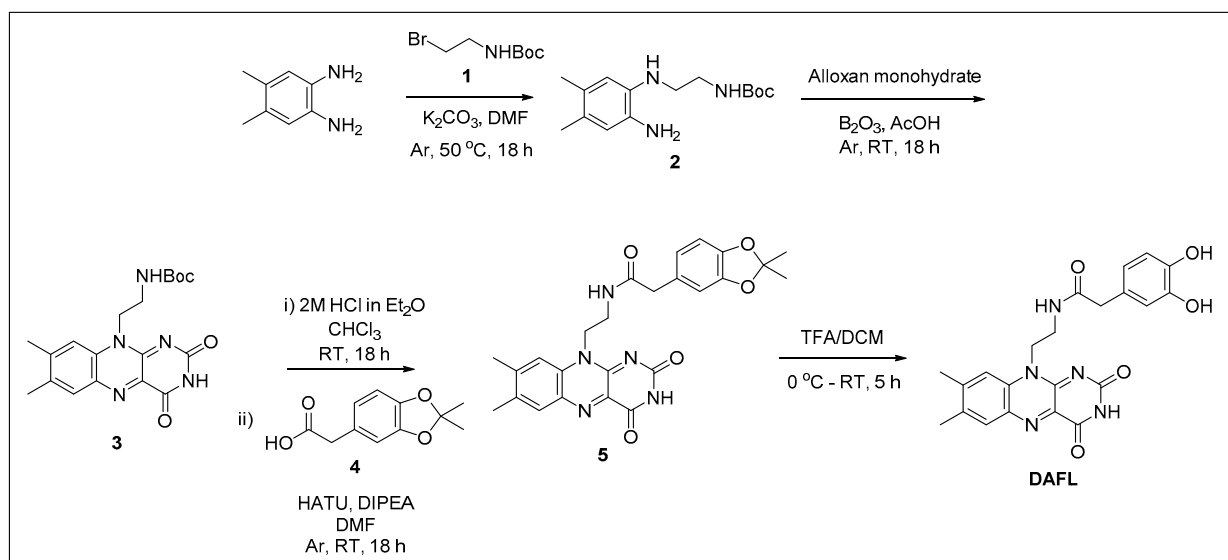


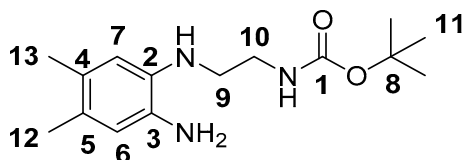
Supplementary Materials: Flavin-conjugated Iron Oxide Nanoparticles as Enzyme-inspired Photocatalysts for Azo Dye Degradation.

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1 Synthesis of Dopamine-Flavin (DAFL):



tert-Butyl (2-((2-amino-4,5-dimethylphenyl)amino)ethyl)carbamate (**2**):



tert-Butyl (2-bromoethyl)carbamate (**1**) was prepared according to the literature procedure by Luescher *et al.*¹

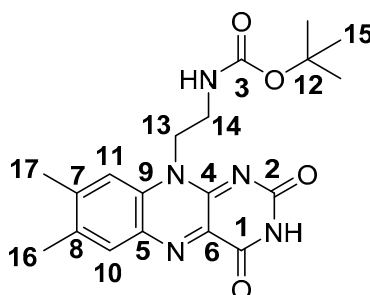
4,5-Dimethylbenzene-1,2-diamine (1.00 g, 7.34 mmol) and K_2CO_3 (2.03 g, 14.68 mmol) were dissolved in anhydrous DMF (40 mL) and heated to 50 °C under Ar atmosphere. A solution of **1** (1.65 g, 7.34 mmol) in anhydrous DMF (10 mL) was then added dropwise and the resulting mixture was stirred at 50 °C overnight. DMF was removed under reduced pressure and the resulting residue was re-dissolved in DCM (50 mL) and washed with water (3 x 50 mL) and brine (2 x 50 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The crude product was then purified by flash column chromatography using the solvent system cyclohexane/ethyl acetate (3:2, v/v) to give the title compound as a red residue (1.05 g, 3.67 mmol, 50%).

^1H NMR (500 MHz, CDCl_3): δ = 6.52 (s, 1H, **H-7**), 6.44 (s, 1H, **H-6**), 4.90 (br. s, 2H, **-NH₂**), 3.39 (br. m, 2H, 2 x **-NH-**), 3.21 (m, 4H, **H-9**, **H-10**), 2.16 (s, 3H, **H-12**), 2.12 (s, 3H, **H-13**) ppm.

^{13}C NMR (500 MHz, CDCl_3): δ = 156.40 (**C-1**), 135.04 (**C-2**), 132.23 (**C-3**), 127.98 (**C-4**), 126.55 (**C-5**), 118.42 (**C-6**), 114.06 (**C-7**), 79.43 (**C-8**), 44.91 (**C-9**), 40.27 (**C-10**), 28.42 (**C-11**), 19.29 (**C-12**), 18.82 (**C-13**) ppm.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{26}\text{O}_2\text{N}_3$ 280.2025; Found 280.2012.

***tert*-Butyl (2-(7,8-dimethyl-2,4-dioxo-3,4-dihydrobenzo[g]pteridin-10(2H)-yl)ethyl)carbamate (3):**



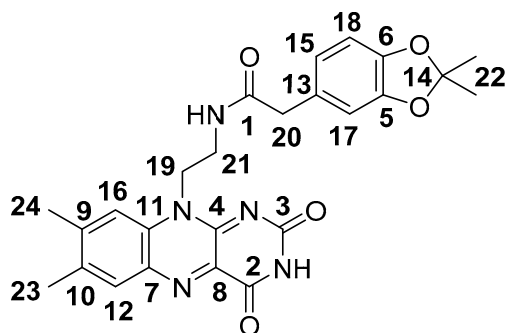
Compound **2** (0.90 g, 3.22 mmol), B_2O_3 (0.45 g, 3.30 mmol) and alloxan monohydrate (0.52 g, 1.65 mmol) were dissolved in glacial acetic acid (10 mL) and left to stir in the dark at room temperature under Ar atmosphere for 18 h. Water was added (10 mL) and extracted with CHCl_3 (3 x 20 mL). The organic layer was evaporated and then co-evaporated with toluene (3 x 20 mL) to remove any traces of water and acetic acid. The residue was then recrystallized from ethanol to afford the title compound as a dark yellow solid (0.66 g, 1.72 mmol, 53%).

^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ = 11.36 (s, 1H, **-CO-NH-CO-**), 7.86 (s, 1H, **H-11**), 7.81 (s, 1H, **H-10**), 6.95 (br. m, 1H, **-CO-NH-CH₂-**), 4.63 (t, 2H, $^3J = 5.5$ Hz, **H-13**), 3.40 (m, 2H, **H-14**), 2.48 (s, 3H, **H-16**), 2.38 (s, 3H, **H-17**), 1.91 (s, 9H, **H-15**) ppm.

^{13}C NMR (500 MHz, $\text{DMSO}-d_6$): δ = 160.07 (**C-1**), 155.94 (**C-2**), 155.72 (**C-3**), 150.44 (**C-4**), 146.59 (**C-5**), 136.77 (**C-6**), 135.92 (**C-7**), 133.99 (**C-8**), 131.60 (**C-9**), 130.99 (**C-10**), 116.30 (**C-11**), 78.04 (**C-12**), 44.37 (**C-13**), 36.97 (**C-14**), 28.02 (**C-15**), 20.90 (**C-16**), 18.81 (**C-17**) ppm.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_4\text{N}_5$ 386.1828; Found 386.1816.

***N*-(2-(7,8-dimethyl-2,4-dioxo-3,4-dihydrobenzo[g]pteridin-10(2H)-yl)ethyl)-2-(2,2-dimethylbenzo[d][1,3]dioxol-5-yl)acetamide (5):**



2-(2,2-Dimethylbenzo[d][1,3]dioxol-5-yl)acetic acid (**4**) was prepared according to the literature procedure by Geiseler *et al.*²

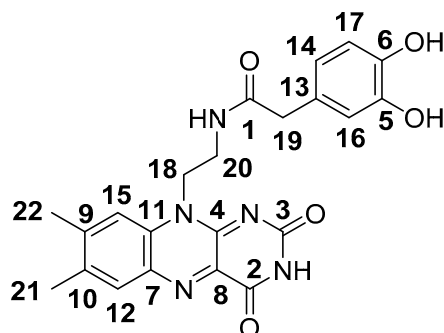
Flavin **3** (170 mg, 0.44 mmol) was dissolved in chloroform (25 mL) and 2M HCl in diethyl ether (3 mL) was added dropwise. The reaction mixture was stirred for 18 h at room temperature and was then concentrated *in vacuo* to yield the hydrochloride salt of flavin **3** as a dark yellow solid (140 mg, 0.44 mmol) which was then dissolved in anhydrous DMF (40 mL) with HATU (200 mg, 0.53 mmol) and DIPEA (0.3 mL, 1.76 mmol) under Ar atmosphere. A solution of **4** (75 mg, 0.36 mmol) in anhydrous DMF (5 mL) was then added to the reaction mixture which was left to stir at room temperature for 18 h. DMF was removed under reduced pressure and the resulting residue was re-dissolved in DCM (50 mL) and washed with water (1 x 30 mL) and brine (3 x 30 mL). The organic layer was then dried over anhydrous Na₂SO₄ and evaporated. The crude product was then purified by column chromatography using the solvent system CHCl₃/MeOH/AcOH (97:2:1, v/v) to give the title compound as an orange solid (86 mg, 0.18 mmol, 50%).

¹H NMR (500 MHz, DMSO-d₆): δ = 11.35 (s, 1H, -CO-NH-CO-), 8.27 (br. m, 1H, -CO-NH-CH₂-), 7.87 (s, 1H, **H-13**), 7.86 (s, 1H, **H-16**), 6.66-6.47 (m, 3H, **H-15**, **H-17**, **H-18**), 4.63 (t, 2H, ³J = 5.5 Hz, **H-19**), 3.47 (m, 2H, **H-21**), 3.16 (s, 2H, **H-20**), 2.46 (s, 3H, **H-23**), 2.38 (s, 3H, **H-24**), 1.60 (s, 6H, **H-22**) ppm.

¹³C NMR (500 MHz, DMSO-d₆): δ = 171.76 (**C-1**), 160.37 (**C-2**), 156.04 (**C-3**), 150.79 (**C-4**), 147.10 (**C-5**), 146.95 (**C-6**), 145.87 (**C-7**), 137.31 (**C-8**), 136.24 (**C-9**), 134.23 (**C-10**), 131.68 (**C-11**), 131.38 (**C-12**), 129.16 (**C-13**), 121.93 (**C-14**), 118.11 (**C-15**), 116.63 (**C-16**), 109.68 (**C-17**), 108.13 (**C-18**), 43.84 (**C-19**), 42.20 (**C-20**), 36.13 (**C-21**), 26.00 (**C-22**), 21.19 (**C-23**), 19.23 (**C-24**) ppm.

HRMS (ESI) m/z: [M + H]⁺ Calcd for C₂₅H₂₆O₅N₅ 476.1928; Found 476.1923.

2-(3,4-Dihydroxyphenyl)-N-(2-(7,8-dimethyl-2,4-dioxo-3,4-dihydrobenzo[g]pteridin-10(2H)-yl)ethyl)acetamide (DAFL):



Flavin **5** (50 mg, 0.105 mmol) was dissolved in DCM (5 mL) and was cooled to 0 °C before adding TFA (1 mL) dropwise. The reaction mixture was then left to stir at room temperature until TLC analysis showed completion (5 h). The solvent and excess TFA were removed under reduced pressure and co-evaporated with toluene (3 x 20 mL) to give the title compound as an orange solid (45 mg, 0.104 mmol, 99%).

^1H NMR (500 MHz, DMSO- d_6): δ = 11.31 (s, 1H, $-\text{CO}-\text{NH}-\text{CO}-$), 8.11 (br. m, 1H, $-\text{CO}-\text{NH}-\text{CH}_2-$), 7.87 (s, 1H, **H-12**), 7.84 (s, 1H, **H-15**), 6.57 (m, 2H, **H-16**, **H-17**), 6.32 (m, 1H, **H-14**), 4.61 (t, 2H, 3J = 6.4 Hz, **H-18**), 3.45 (m, 2H, **H-20**), 3.09 (s, 2H, **H-19**), 2.45 (s, 3H, **H-21**), 2.39 (s, 3H, **H-22**) ppm.

^{13}C NMR (500 MHz, DMSO- d_6): δ = 172.18 (**C-1**), 160.37 (**C-2**), 156.06 (**C-3**), 150.76 (**C-4**), 146.94 (**C-5**), 145.36 (**C-6**), 144.30 (**C-7**), 137.36 (**C-8**), 134.24 (**C-9**), 134.25 (**C-10**), 131.38 (**C-11**), 131.38 (**C-12**), 126.82 (**C-13**), 120.15 (**C-14**), 116.87 (**C-15**), 116.57 (**C-16**), 115.75 (**C-17**), 43.71 (**C-18**), 42.16 (**C-19**), 36.07 (**C-20**), 21.24 (**C-21**), 19.23 (**C-22**) ppm.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_5\text{N}_5$ 434.1464; Found 434.1466.

Sample	Hydrodynamic Size (nm)	PDI	Zeta Potential (mV)	Average TEM Size (nm)
IONP	152.3±2.45	0.211±0.014	-19.25±4.51	12.38±1.12
IONP-DA	196.4±4.72	0.320±0.015	27.0±0.22	17.69±0.94
IONP-DAFL	209.5±1.4	0.320±0.014	19.5±1.04	16.17±0.85

Table S1. DLS and zeta potential measurements of IONP, IONP-DA, and IONP-DAFL samples. The errors are calculated from the standard deviation of 3 repeats. Sizes from TEM images are the average of the particle size distribution of 100 particles of each sample. The error is the standard deviation.

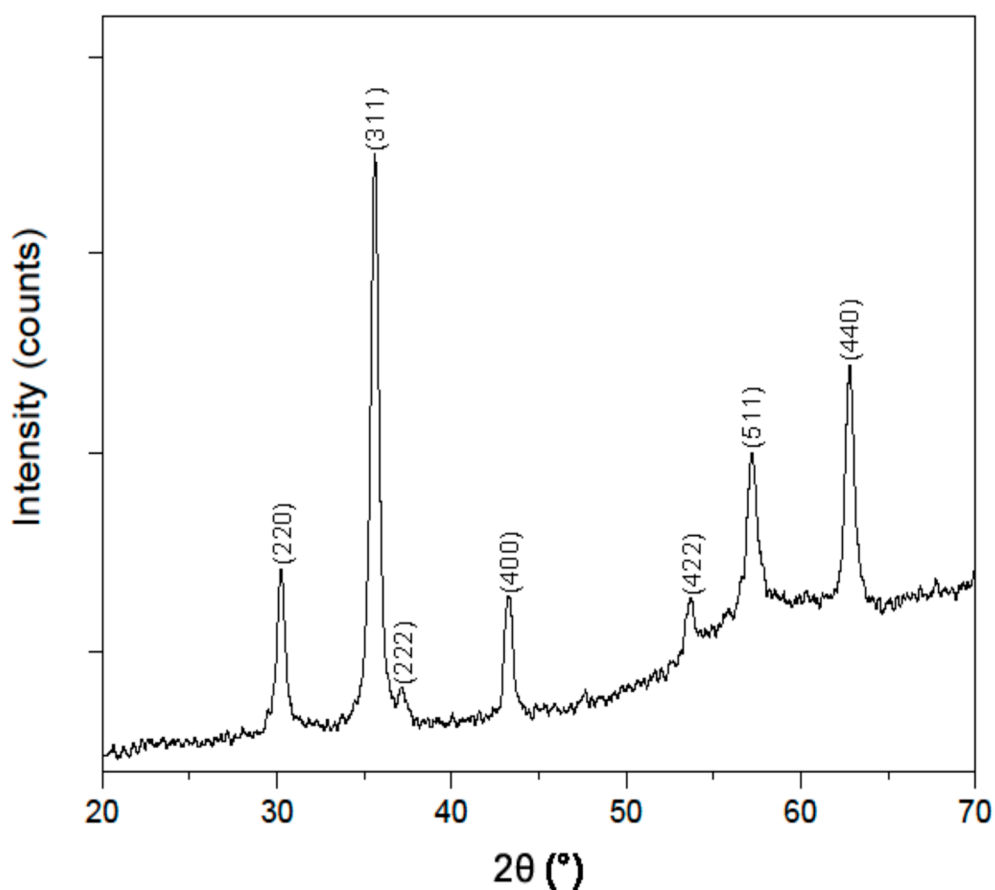


Figure S1. X-ray diffraction spectroscopy pattern of the γ -Fe₂O₃ IONPs.

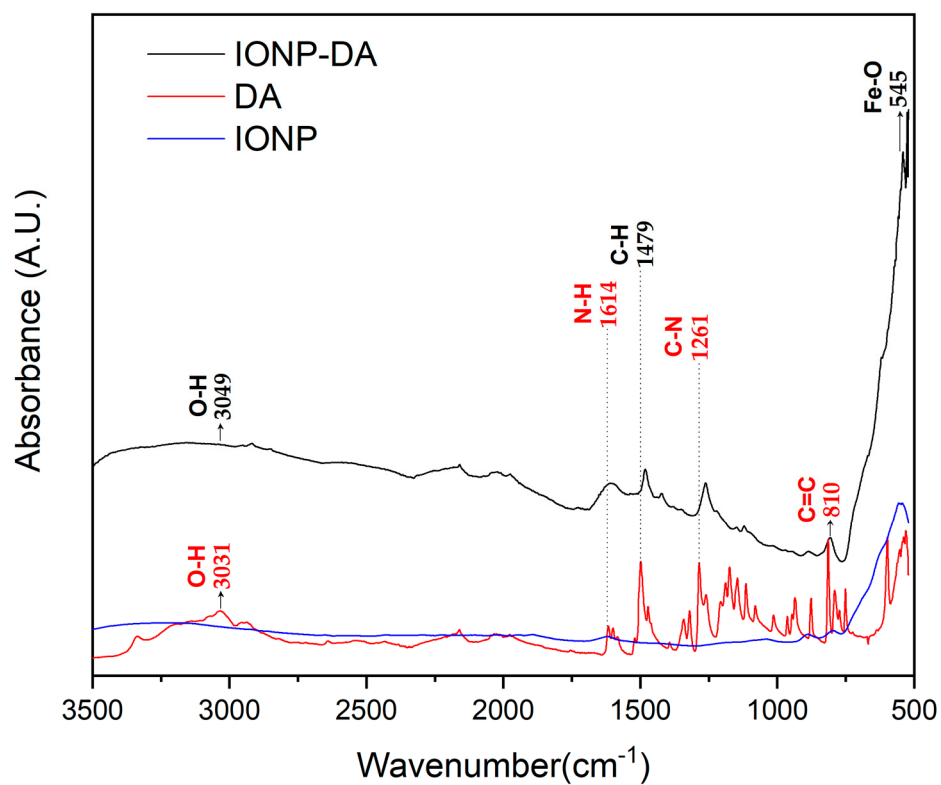


Figure S2. The ATR-FTIR spectrum of γ -Fe₂O₃ IONPs functionalized with dopamine (IONP-DA) in comparison to IONP and dopamine (DA).

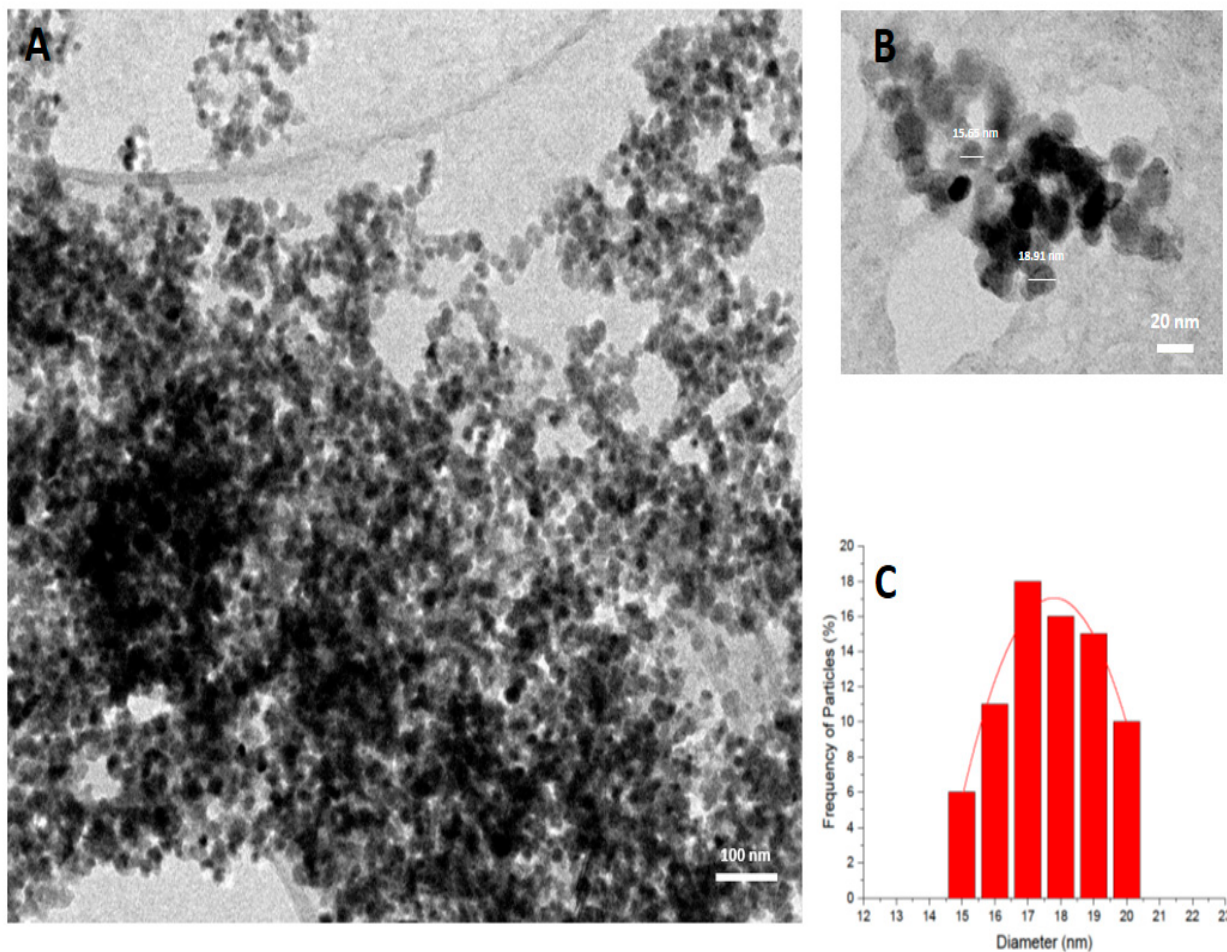


Figure S3. TEM images of IONP-DA at a scale of **(A)** 100nm and **(B)** 20nm. **(C)** The particle size distribution determined from the average of ~100 measurements of particles.

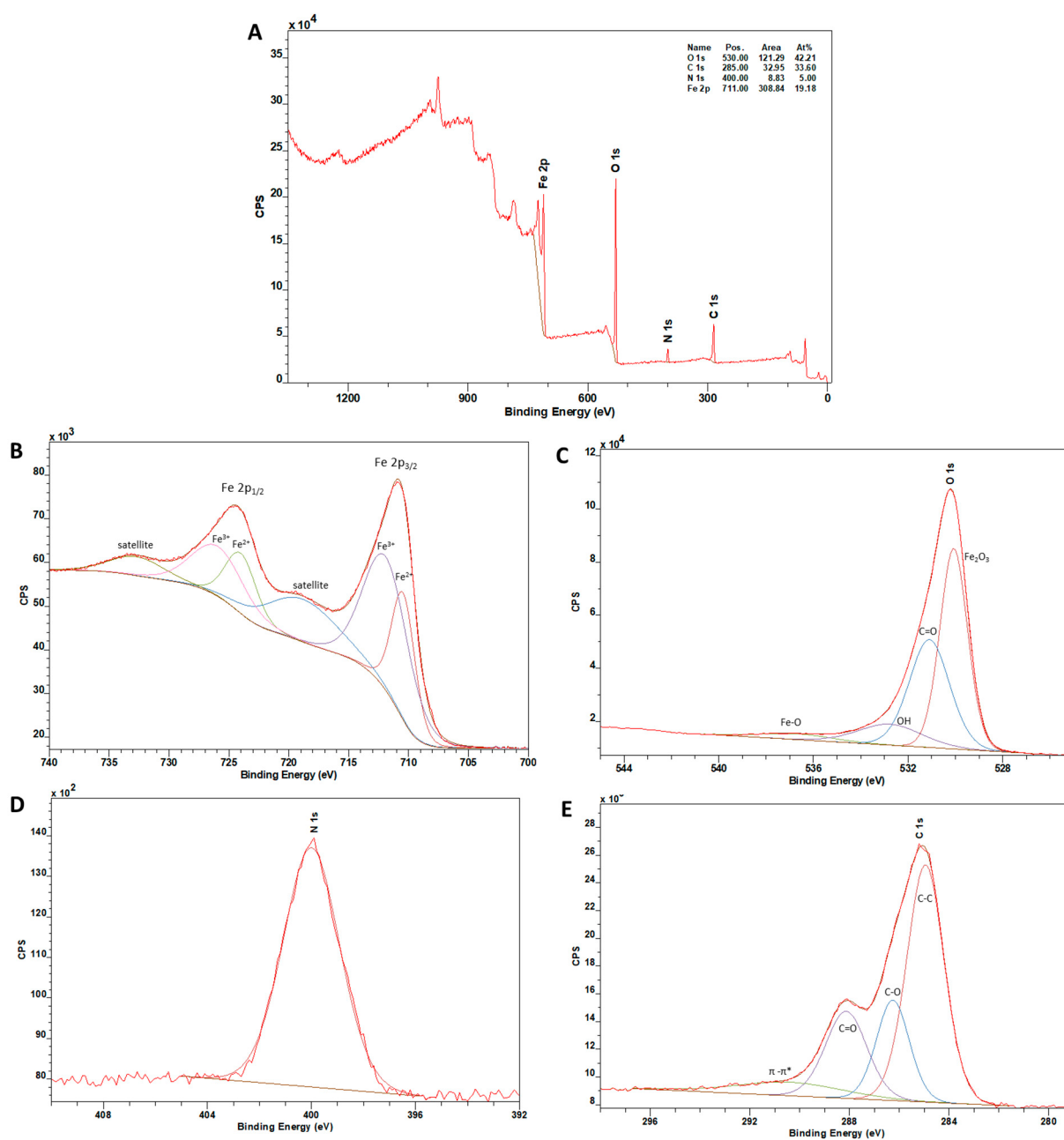


Figure S4: (A) XPS survey of IONP-DAFL and associated spectra: (B) Fe 2p high resolution scan, (C) O 1s high resolution scan, (D) N 1s high resolution scan, and (E) C 1s high resolution scan.

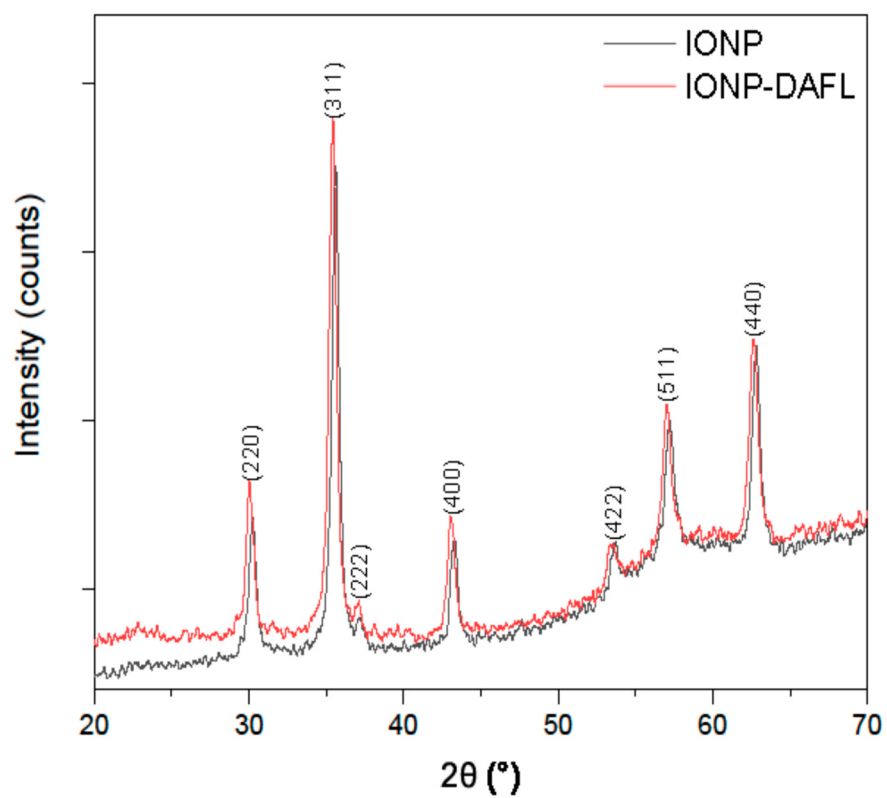


Figure S5. X-ray diffraction spectroscopy pattern of the IONP-DAFL in comparison to IONP

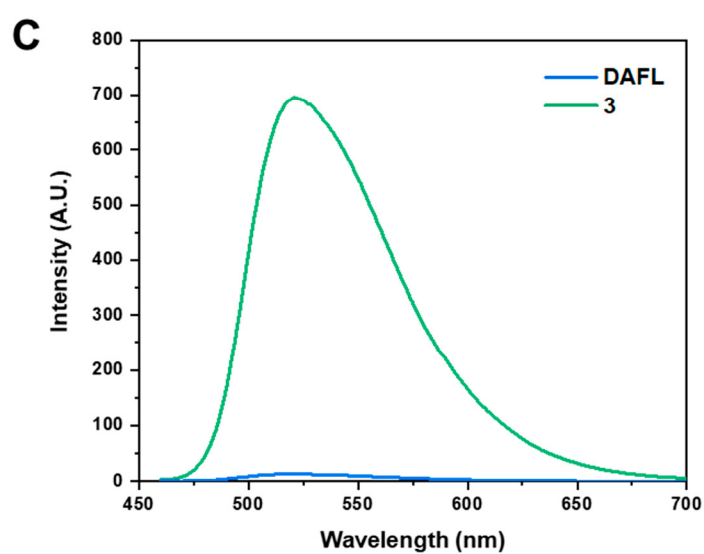
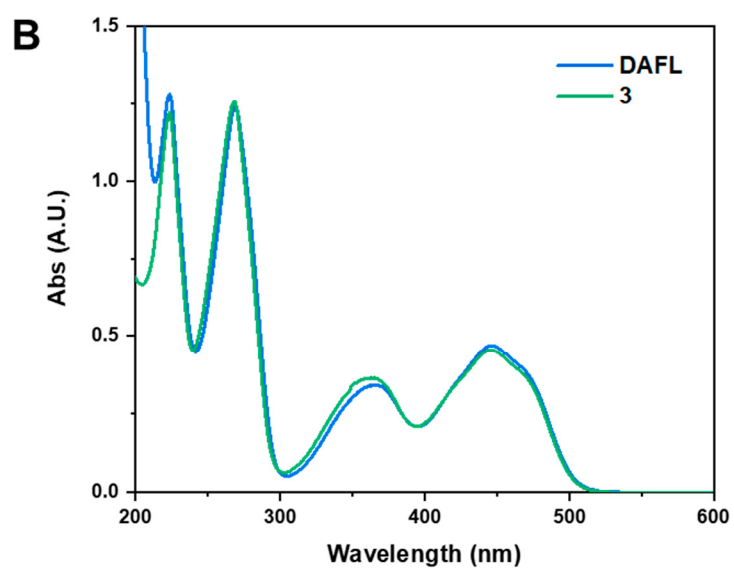
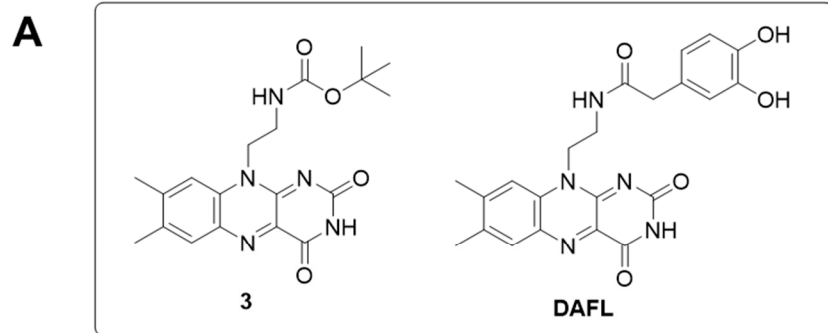


Figure S6. (A) Molecular structure of NBoc-flavin (**3**) and DAFL, (B) their UV absorption spectrum, and (C) fluorescence emission intensity.

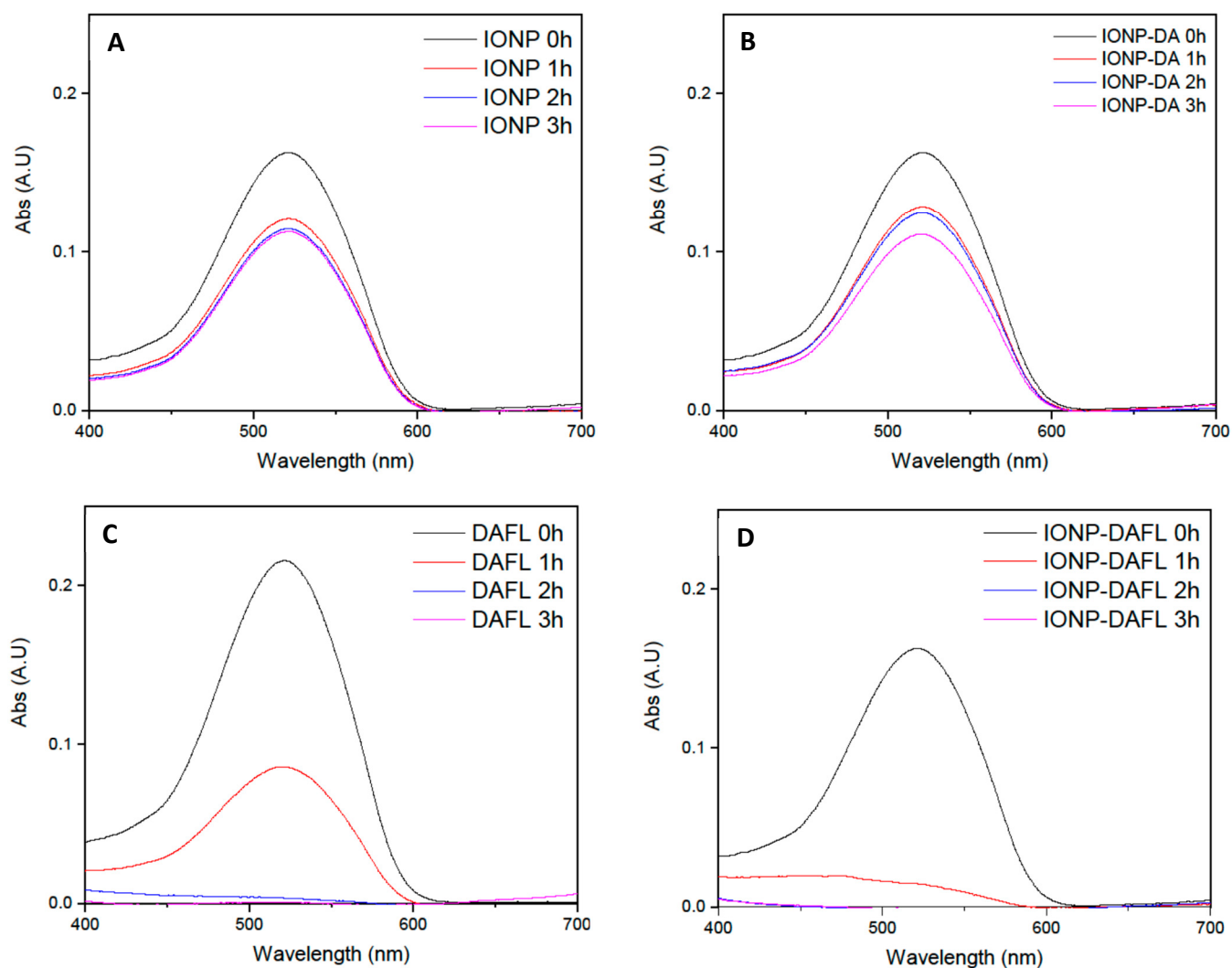


Figure S7. UV-Vis absorption spectroscopy measurements of AMT ($\lambda_{\text{max}} = 520\text{nm}$) after irradiation with 450 nm blue light for 3 hours in the presence of (A) IONP, (B) IONP-DA, (C) DAFL, or (D) IONP-DAFL in MES (0.1 M) under an O_2 atmosphere.

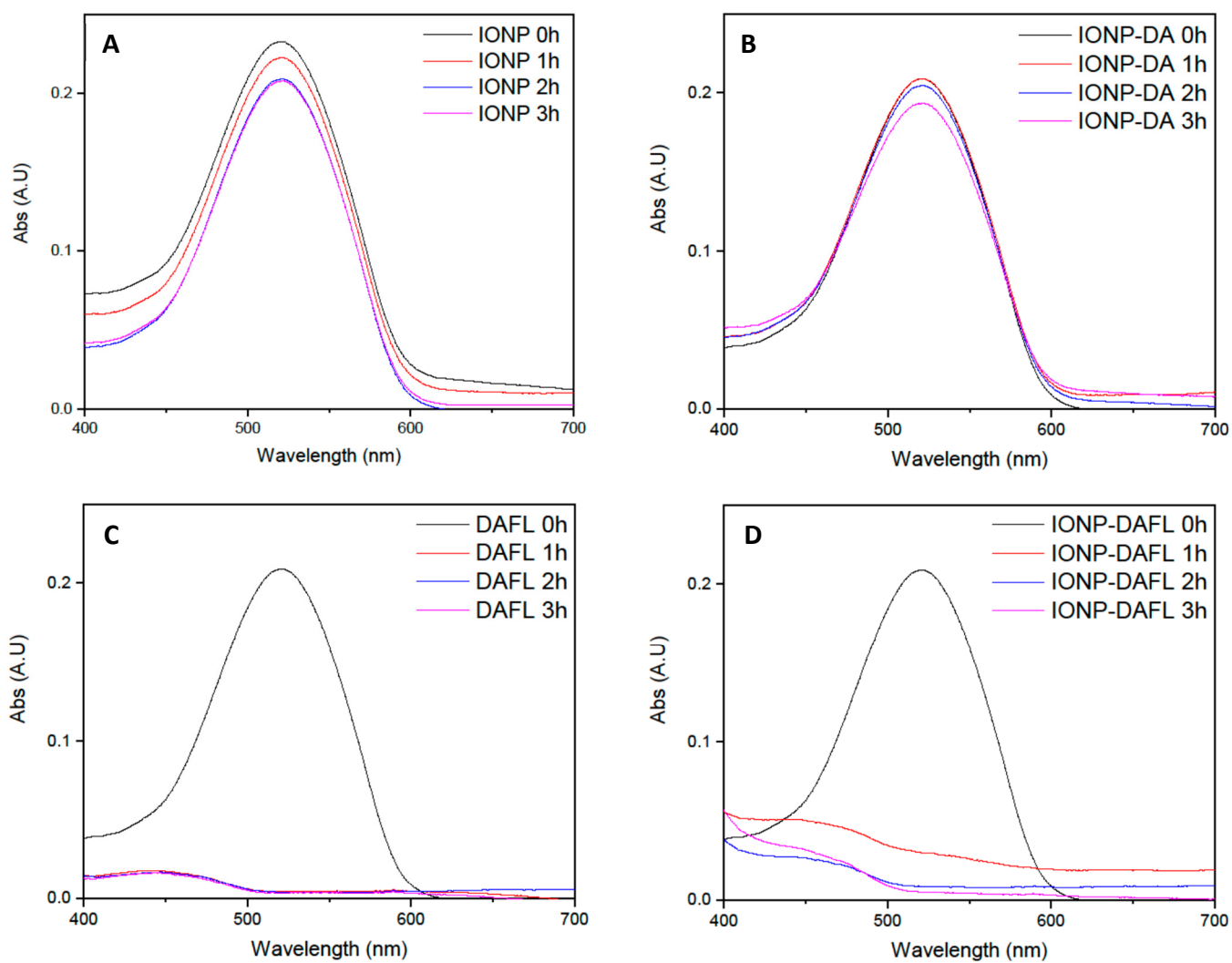


Figure S8. UV-Vis absorption spectroscopy measurements of AMT ($\lambda_{\text{max}} = 520\text{nm}$) after irradiation with 450 nm blue light for 3 hours in the presence of (A) IONP, (B) IONP-DA, (C) DAFL, or (D) IONP-DAFL in EDTA (0.1 M) under an O_2 atmosphere.

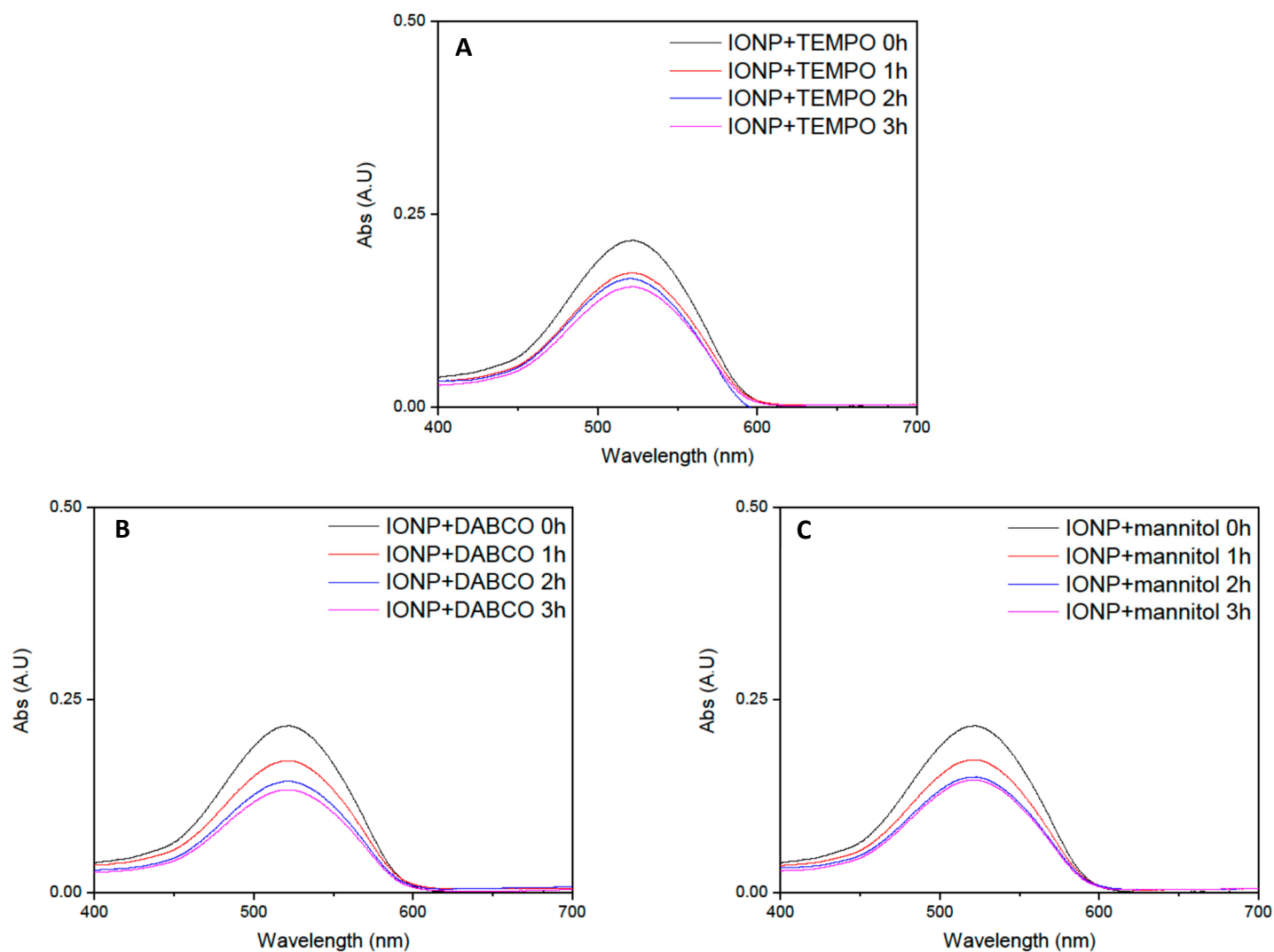


Figure S9. UV-Vis absorption spectroscopy measurements of AMT ($\lambda_{\text{max}} = 520\text{nm}$) after irradiation with 450 nm blue light for 3 hours in the presence of (A) IONP+TEMPO, (B) IONP+DABCO, or (C) IONP+mannitol in MES (0.1 M) under an O_2 atmosphere.

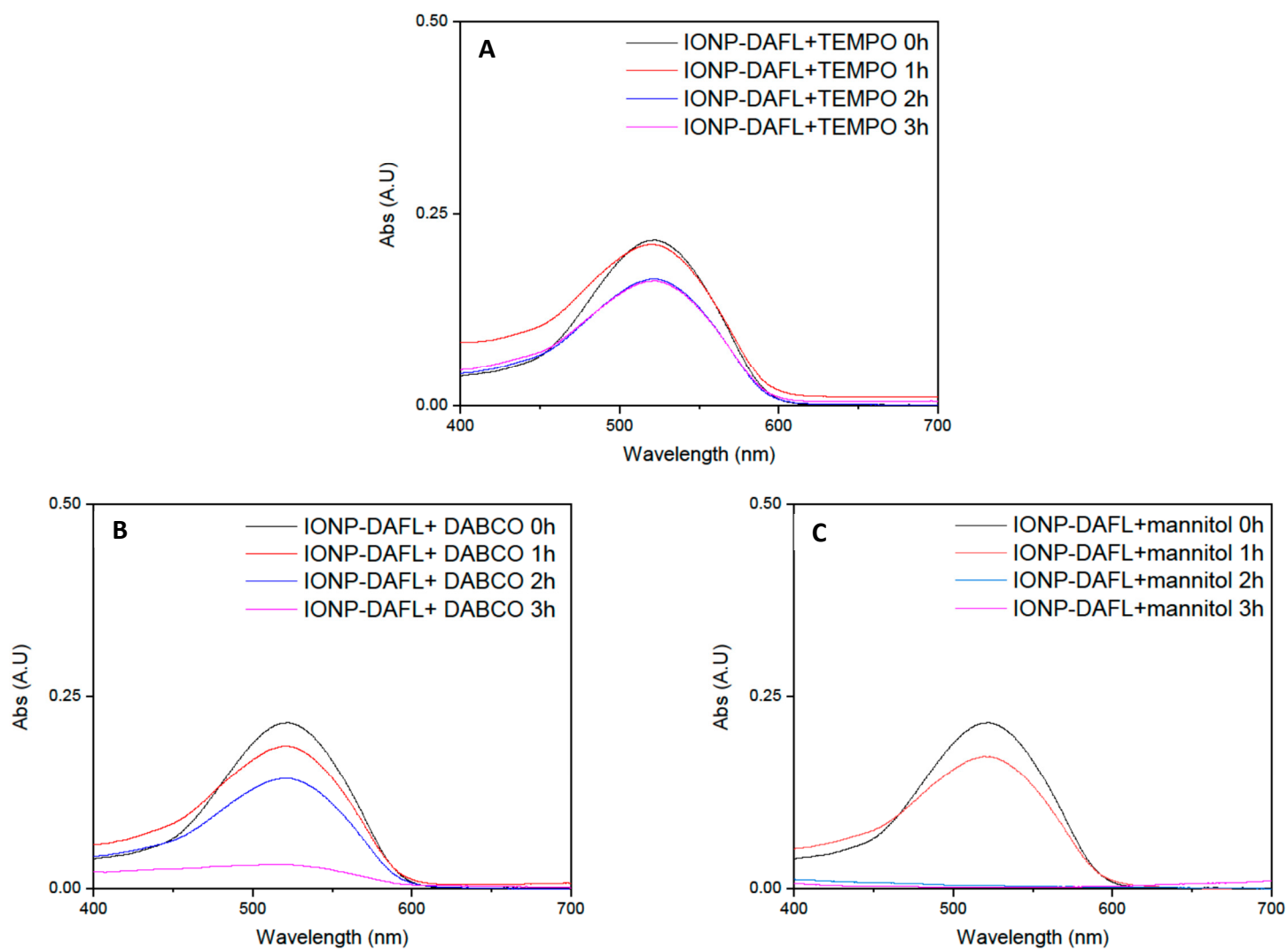


Figure S10. UV-Vis absorption spectroscopy measurements of AMT ($\lambda_{\text{max}} = 520\text{nm}$) after irradiation with 450 nm blue light for 3 hours in the presence of (A) IONP-DAFL+TEMPO, (B) IONP-DAFL+DABCO, or (C) IONP-DAFL+mannitol in MES (0.1 M) under an O_2 atmosphere.

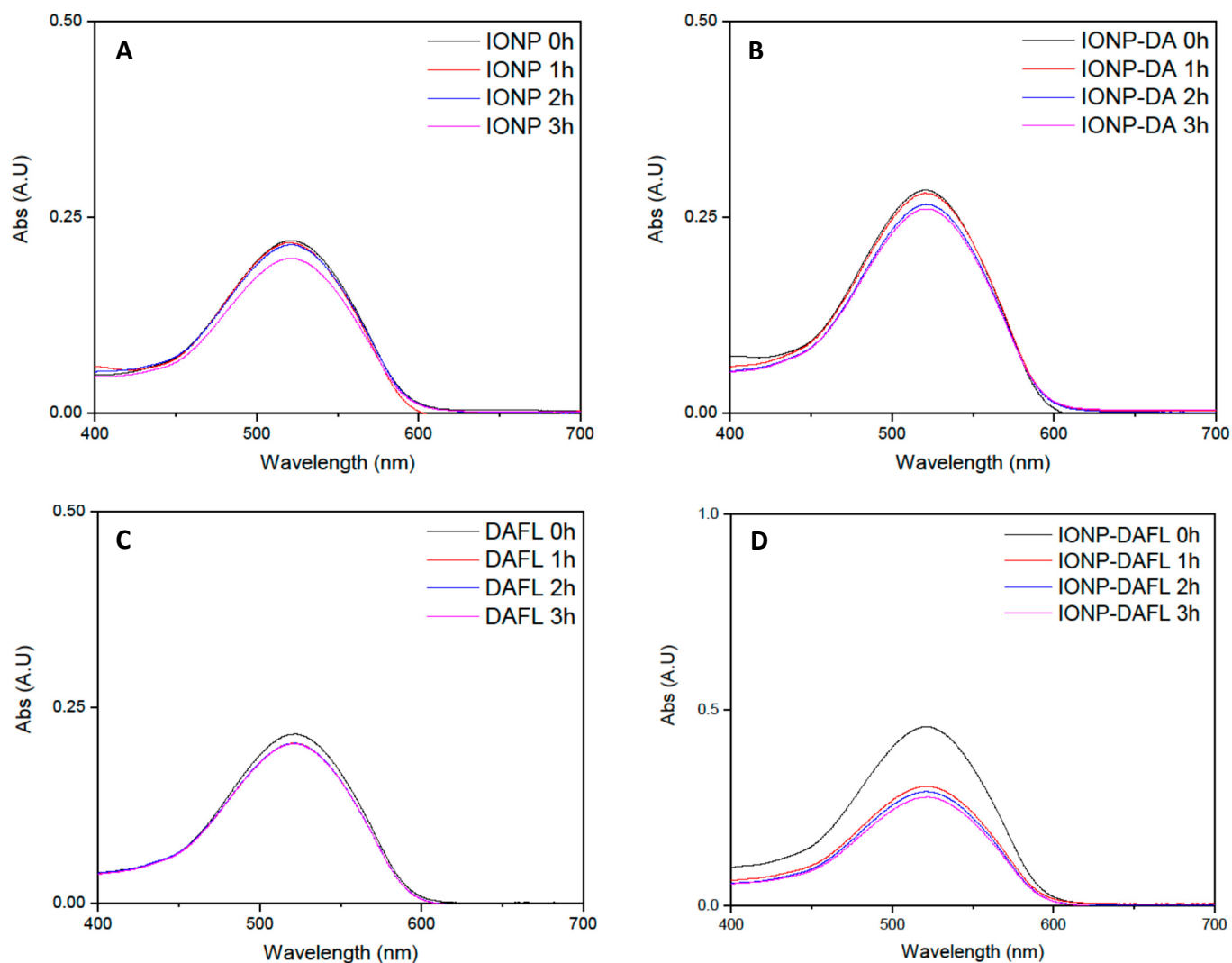


Figure S11. UV-Vis absorption spectroscopy measurements of AMT ($\lambda_{\text{max}} = 520\text{nm}$) after irradiation with 450 nm blue light for 3 hours in the presence of (A) IONP, (B) IONP-DA, (C) DAFL, or (D) IONP-DAFL in MES (0.1 M) under an Ar atmosphere.

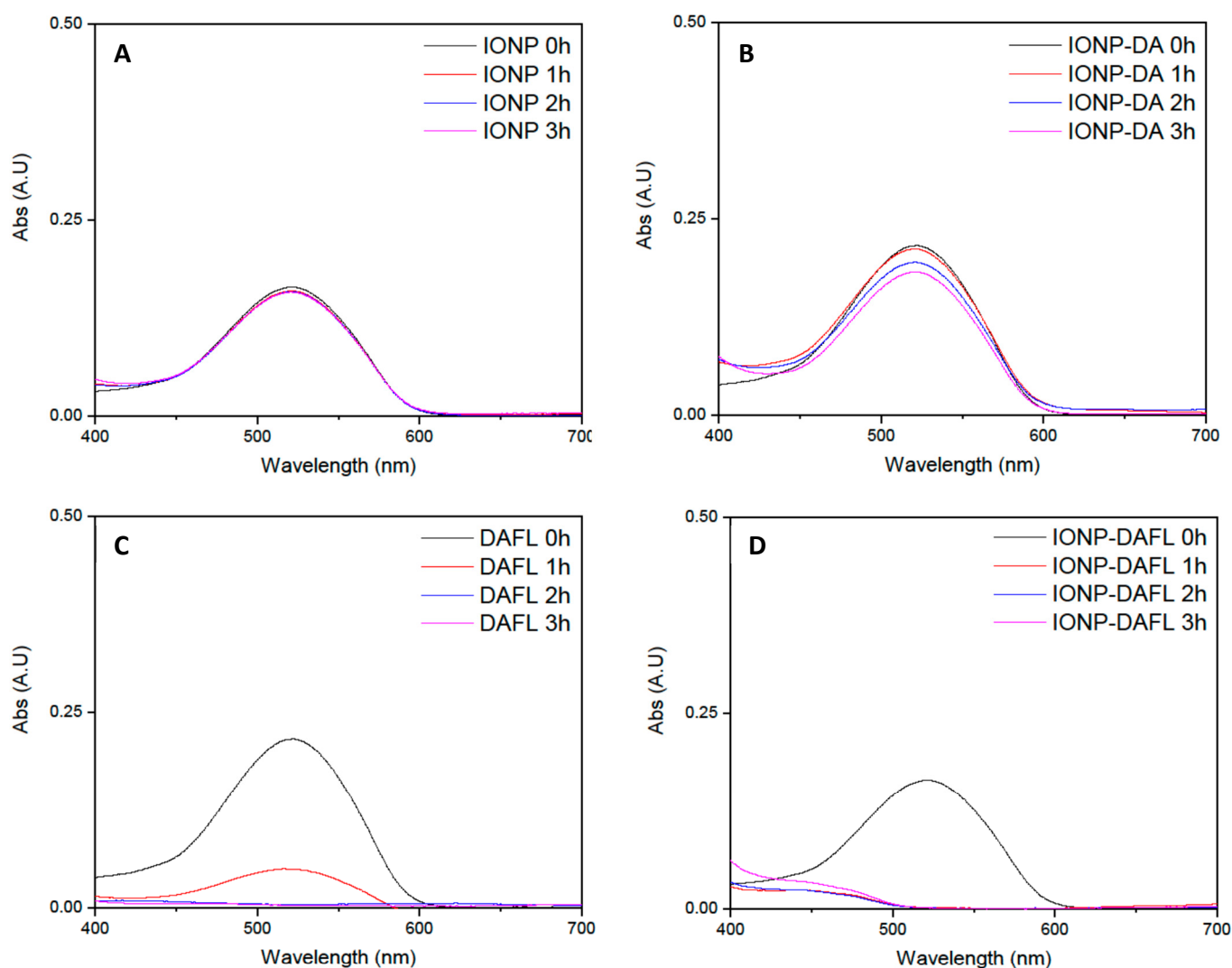


Figure S12. UV-Vis absorption spectroscopy measurements of AMT ($\lambda_{\text{max}} = 520 \text{ nm}$) after irradiation with 450 nm blue light for 3 hours in the presence of (A) IONP, (B) IONP-DA, (C) DAFL, or (D) IONP-DAFL in EDTA (0.1 M) under an Ar atmosphere.

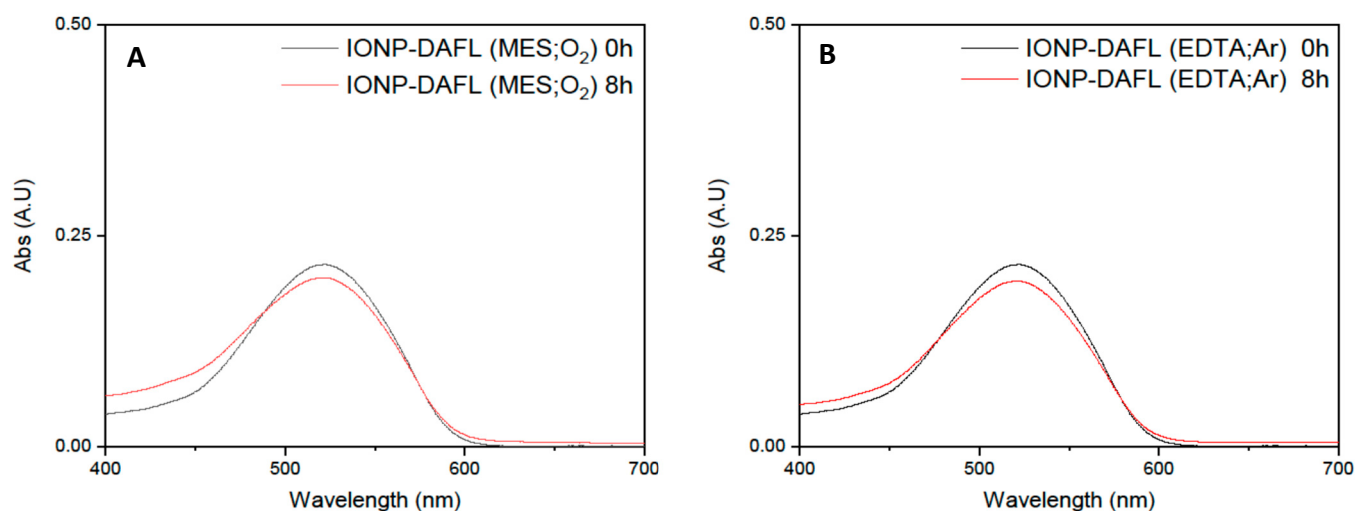


Figure S13. UV-Vis absorption spectroscopy measurements of AMT ($\lambda_{\text{max}} = 520 \text{ nm}$) after being kept in the dark for 8 hours in the presence of (A) IONP-DAFL in MES (0.1 M) under an O_2 atmosphere and (B) IONP-DAFL in EDTA (0.1 M) under an Ar atmosphere.

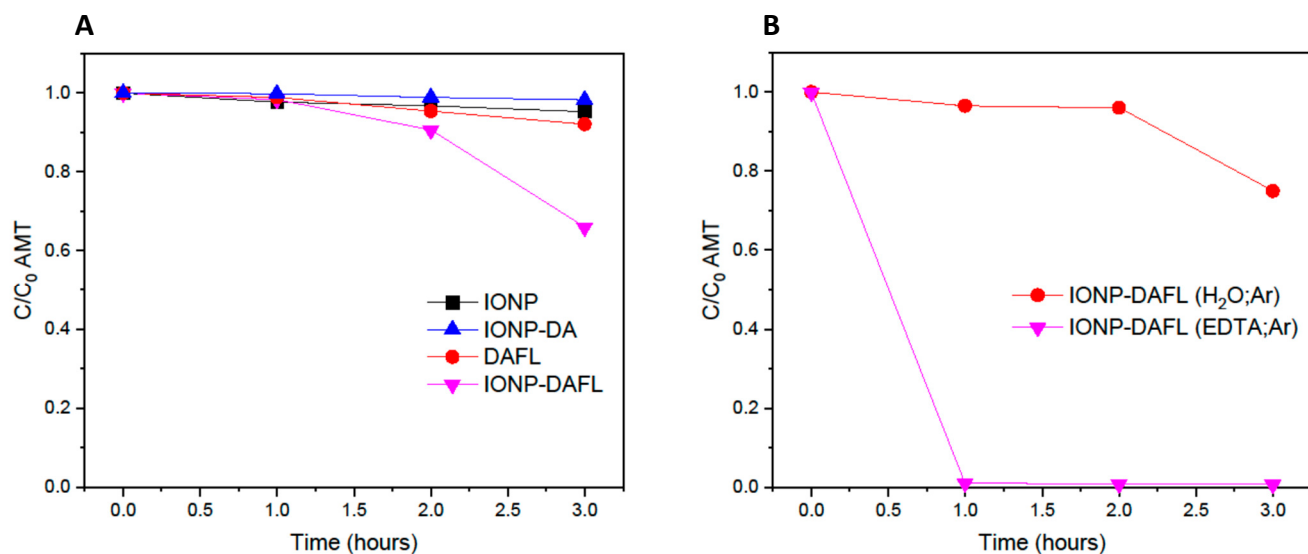


Figure S14. (A) The relative concentration of remaining AMT in solution (C/C_0) measured using UV-vis absorption spectroscopy ($\lambda_{\max} = 520\text{nm}$) after irradiation with 450nm blue light for 3 hours in the presence of IONP, IONP-DA, DAFL, or IONP-DAFL in the absence of an electron donor (ED) in an O_2 atmosphere. (B) The relative concentration of remaining AMT in solution (C/C_0) measured using UV-vis absorption spectroscopy ($\lambda_{\max} = 520\text{nm}$) after irradiation with 450nm blue light for 3 hours in the presence of IONP-DAFL in the absence of an electron donor (ED) in comparison to EDTA as an electron donor (ED) under an inert Ar environment.

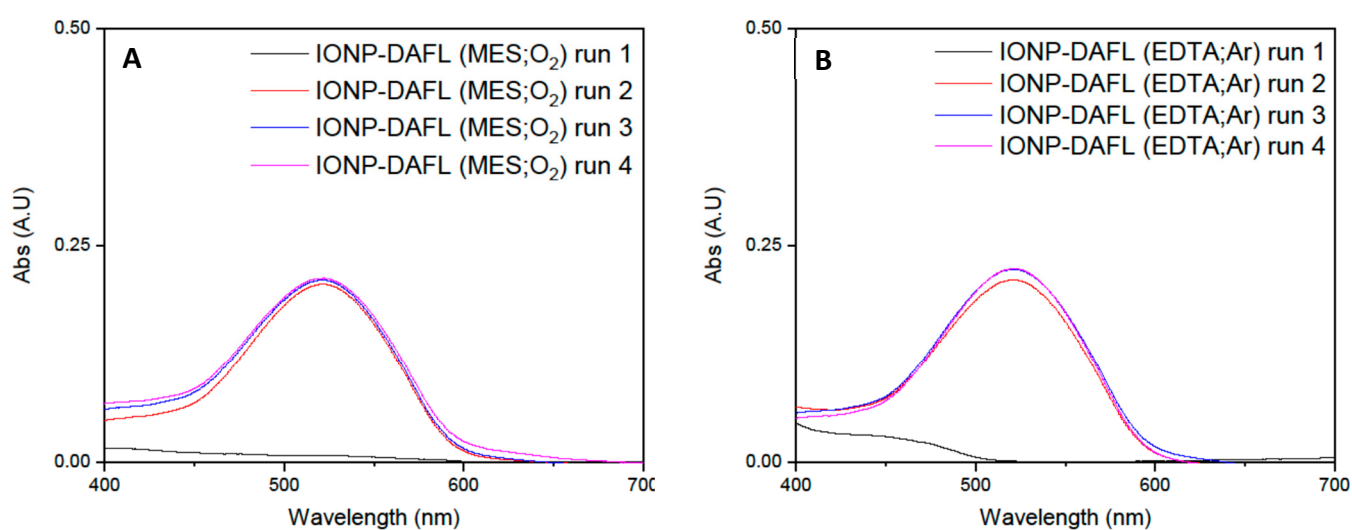


Figure S15. UV-Vis absorption spectroscopy measurements of AMT ($\lambda_{\max} = 520\text{nm}$) after irradiation with 450 nm blue light for 1 hour per run for 4 runs in the presence of (A) IONP-DAFL in MES (0.1 M) under an O_2 atmosphere and (B) IONP-DAFL in EDTA (0.1 M) under an Ar atmosphere.

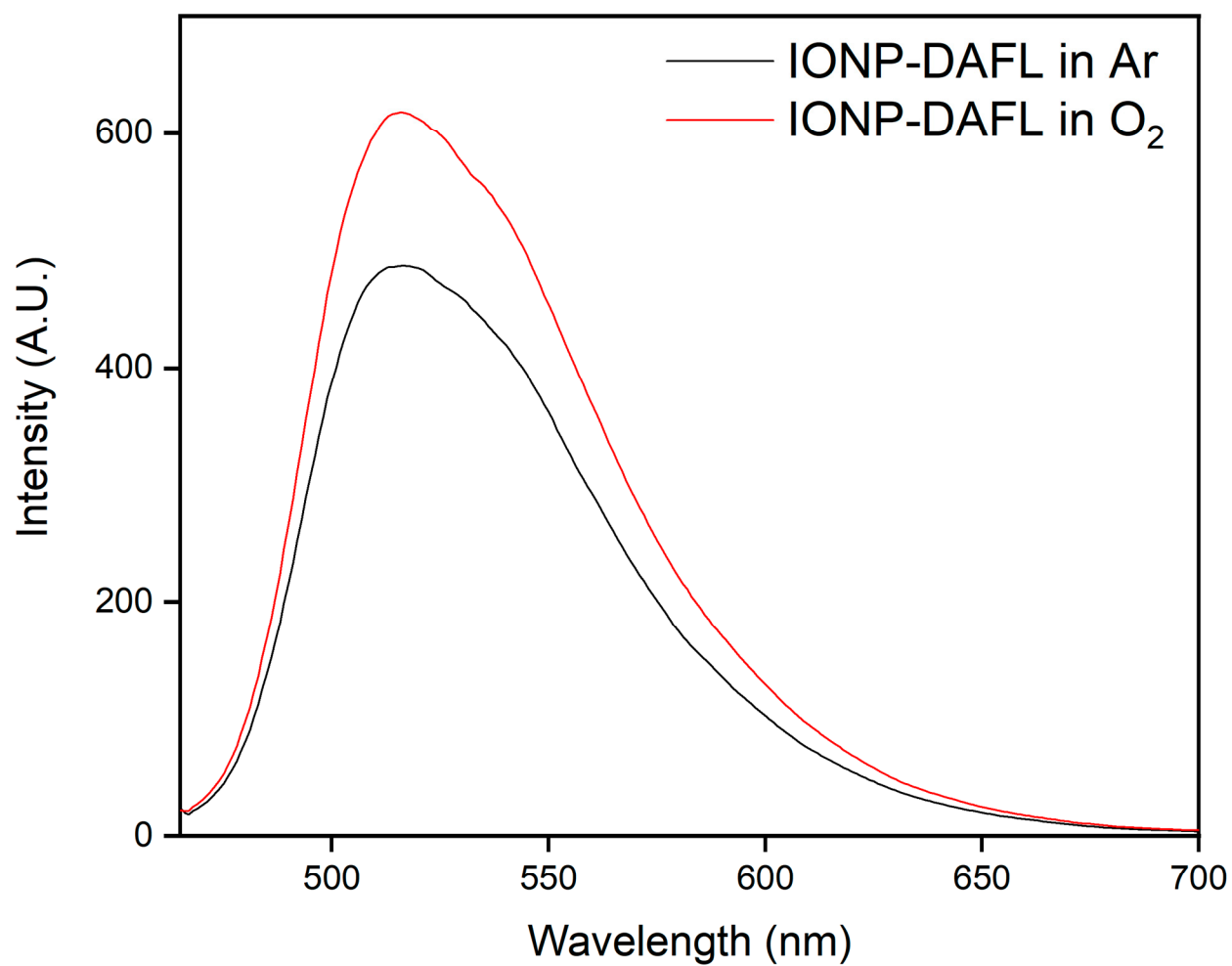


Figure S16. Fluorescence intensity measurements of aliquots taken from the supernatant of IONP-DAFL after irradiation with blue light in O₂ or Ar for 1 hour ($\lambda_{\text{ex}} = 450$ nm).

Quantum Efficiency

The quantum efficiency of AMT degradation was estimated by first calculating the energy of 450 nm photons produced by the LED used to irradiate the reaction using the Planck-Einstein relation (4.414×10^{-19} J). Then the total energy per second was calculated to be 0.102 Js^{-1} using the irradiance of the LED used in the photoreactor (34 mW/cm^2) and the area of the reaction mixture in the vial (3 cm^2). The number of photons per second emitted by the LED can then be calculated using these values (2.311×10^{17} photons/s). Finally, the quantum efficiency (QE) was then estimated using the reaction rate constant divided by the number of photons per second:

Reaction	Rate (s^{-1})	QE
IONP-DAFL (MES, O_2)	3.45×10^{-4}	1.493×10^{-21}
IONP-DAFL (EDTA, Ar)	1.36×10^{-3}	5.884×10^{-21}

The rates of the reactions of IONP-DAFL (MES, O_2) and IONP-DAFL (EDTA, Ar) are calculated by finding the slope of the tangent to the best fit curve of each data set as shown below. The rate is then converted from h^{-1} to s^{-1} .

