

Scheme S1. Structures of  $n$ PUA ( $n=1, 2$  and  $9$ ).

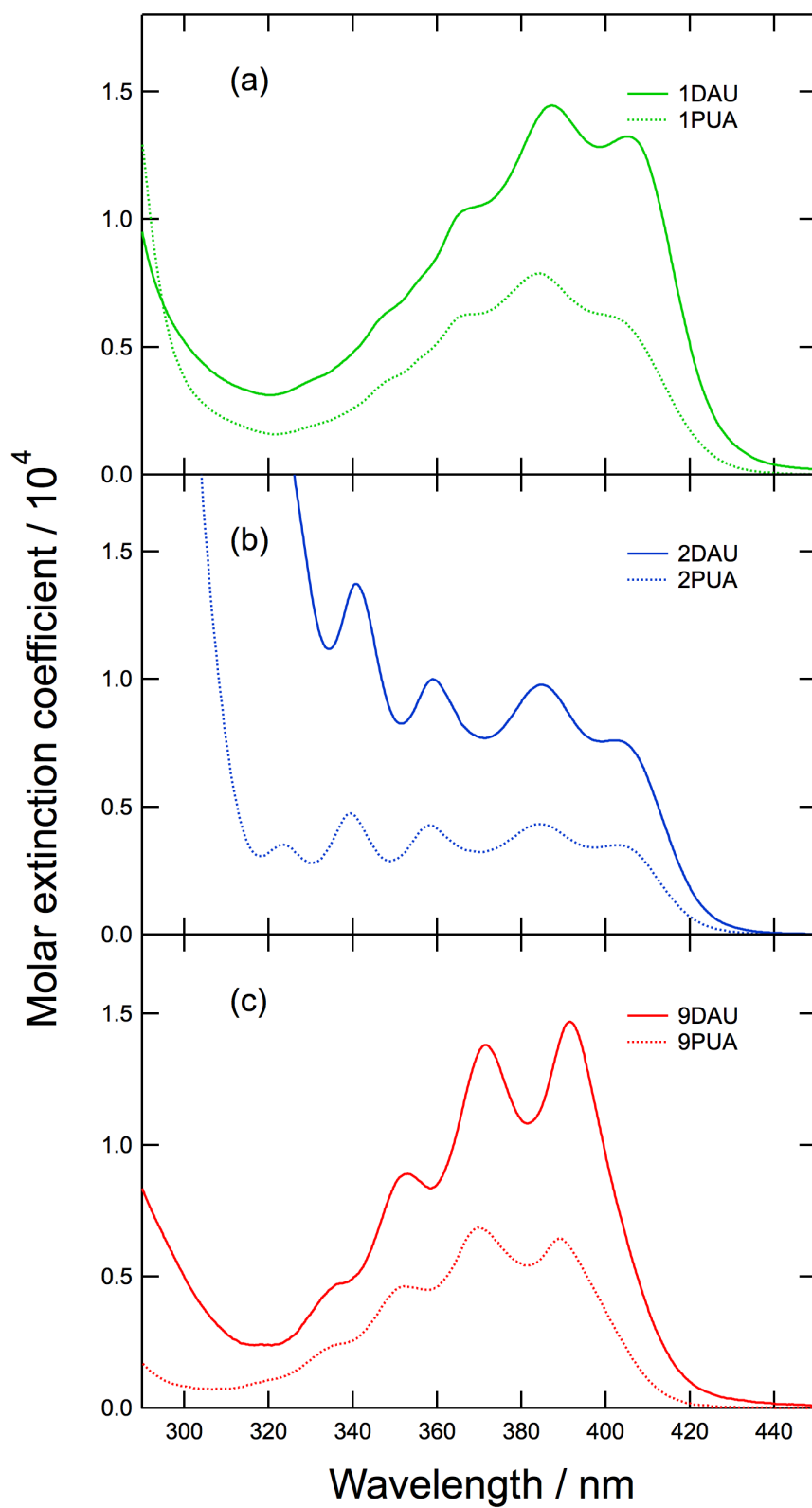


Figure S1. Absorption spectra of (a) 1DAU and 1PUA, (b) 2DAU and 2PUA, and (c) 9DAU and 9PUA in DMSO under Ar.

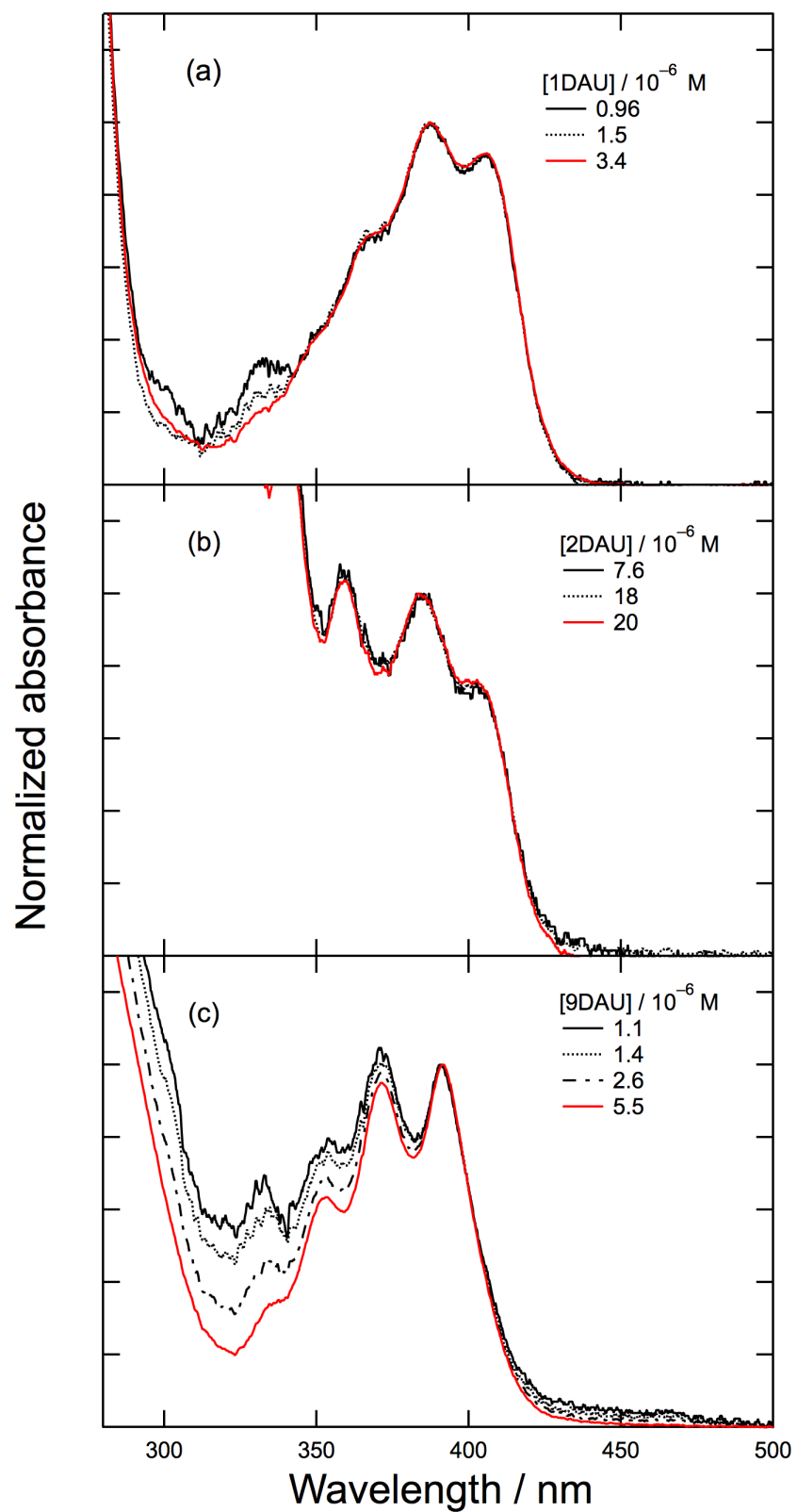


Figure S2. Concentration dependence of absorption spectra (a) 1DAU, (b) 2DAU and (c) 9DAU in DMSO under Ar.

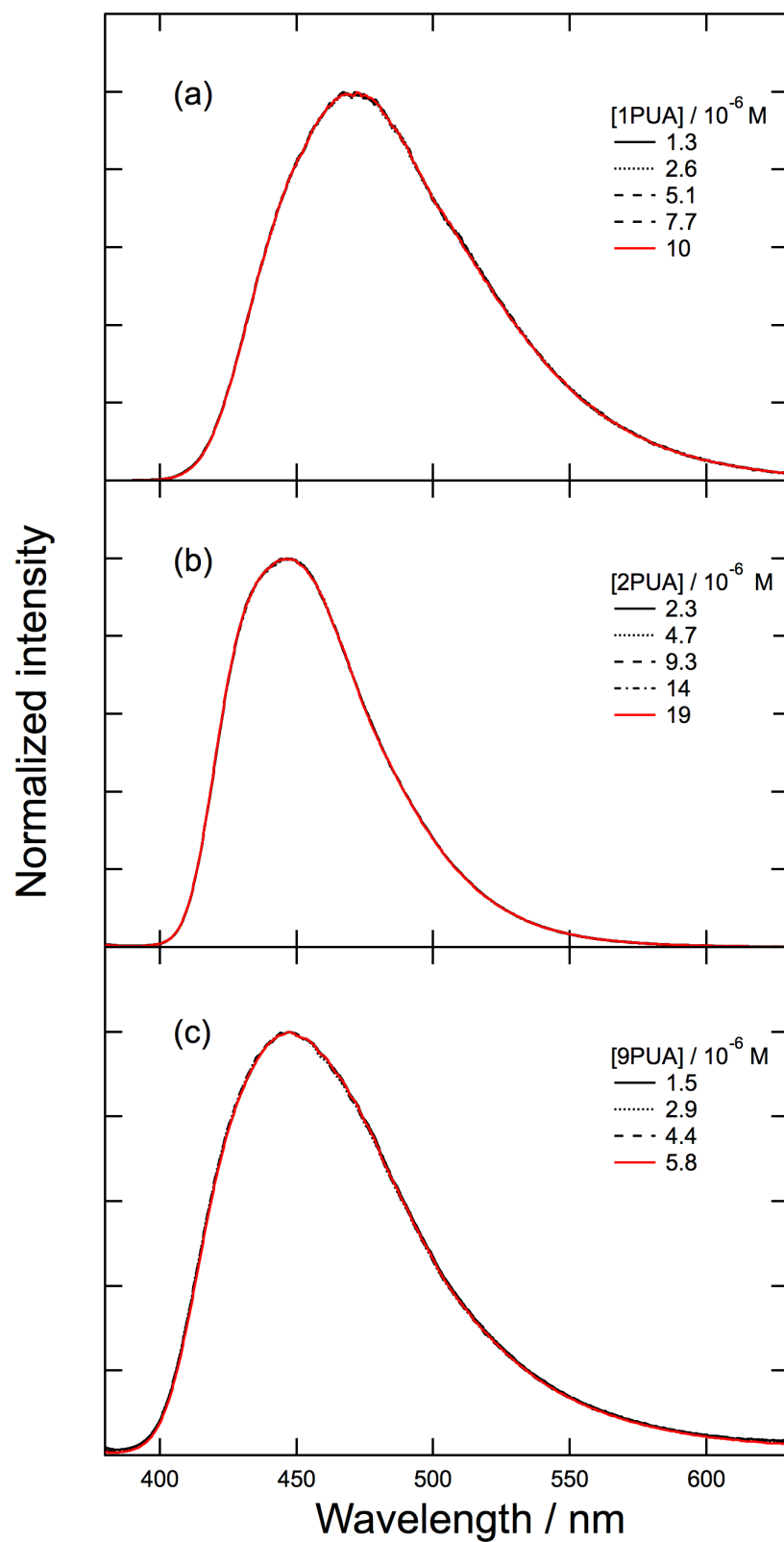


Figure S3. Concentration dependence of fluorescence spectra of (a) 1PUA, (b) 2PUA and (c) 9PUA in DMSO under Ar.

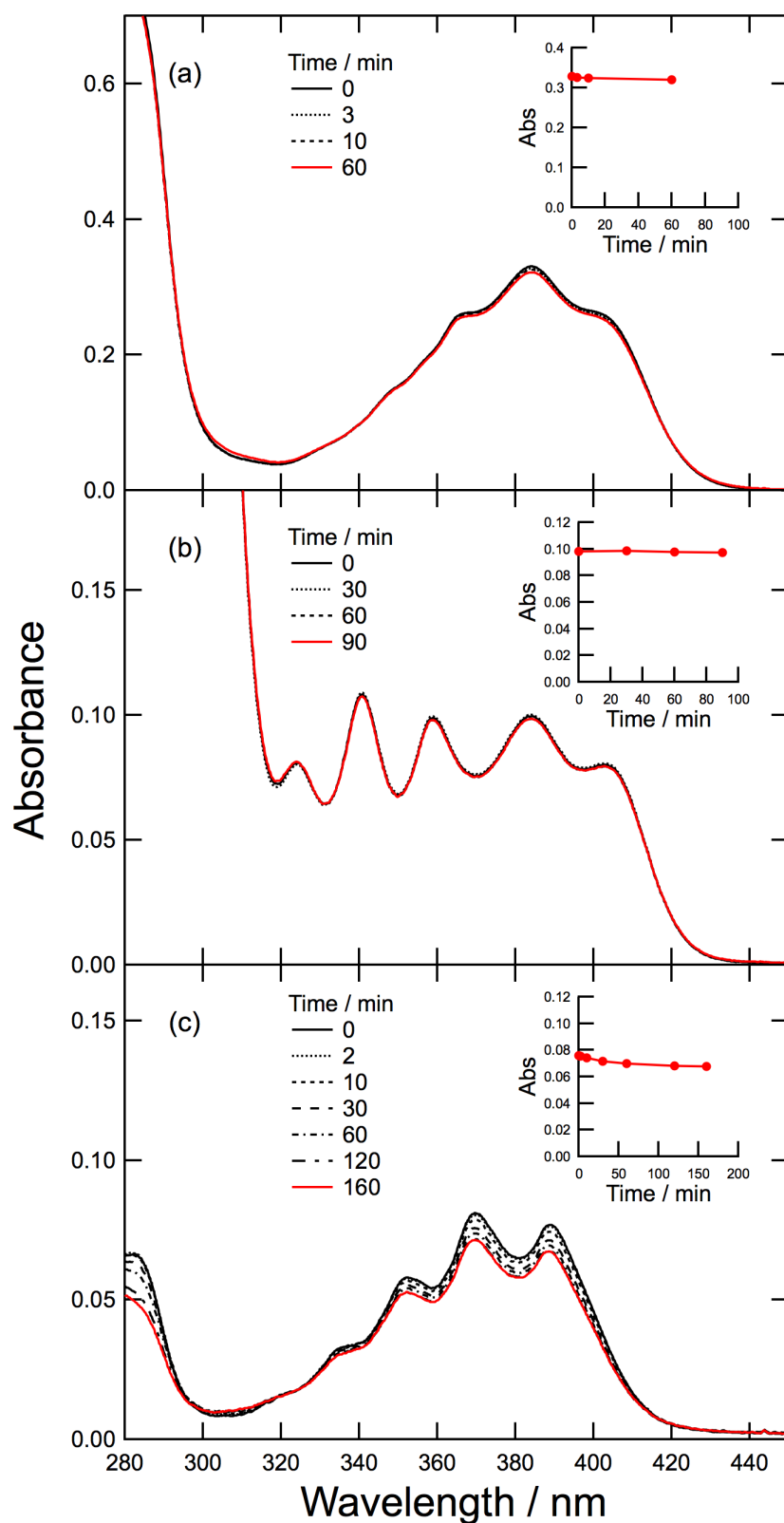


Figure S4. Changes in absorption spectra of (a) 1PUA, (b) 2PUA and (c) 9PUA with irradiation at 365 nm in DMSO under Ar.

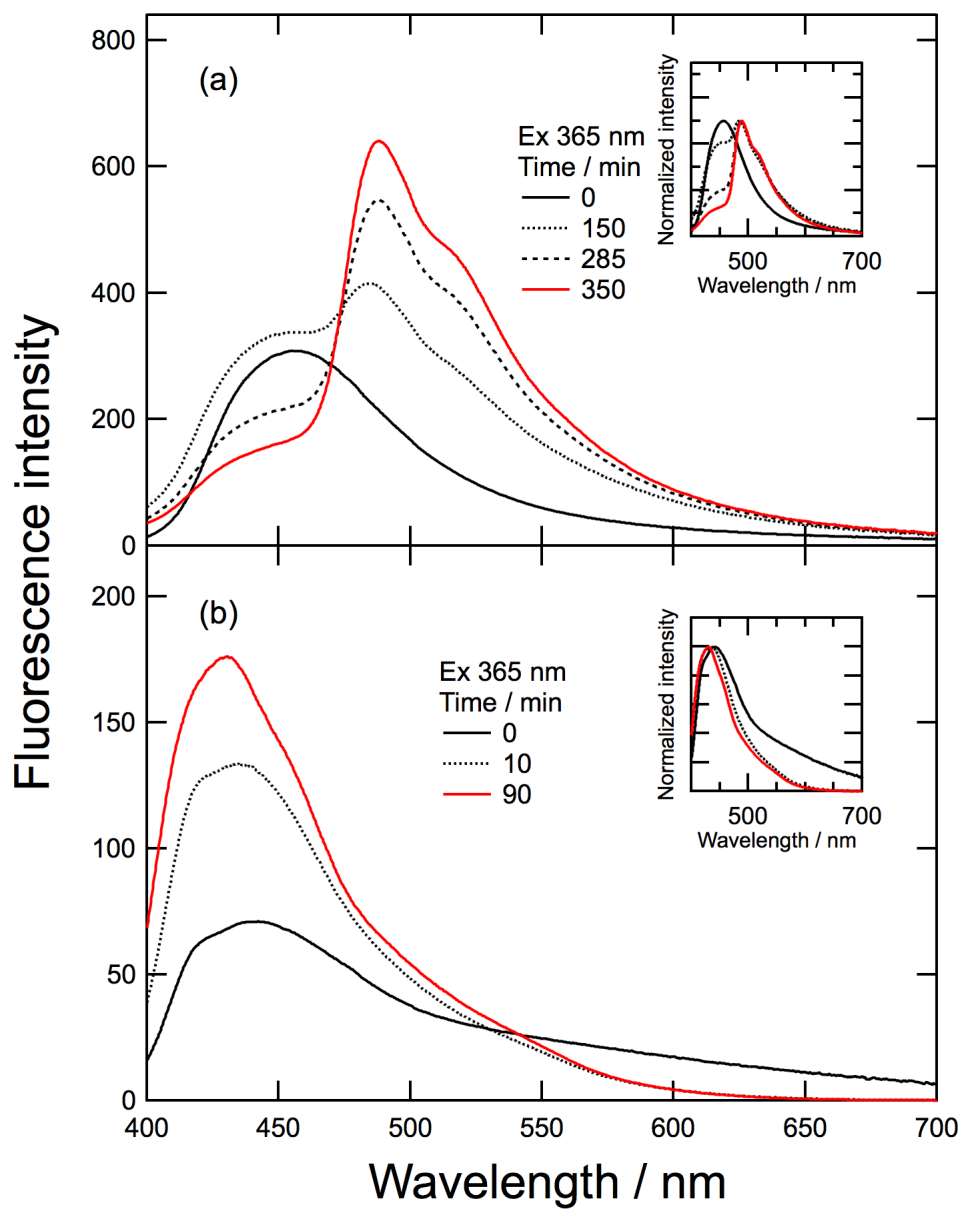


Figure S5. Changes in fluorescence spectra of (a) 1DAU and (b) 9DAU with irradiation at 365 nm in DMSO under Ar.

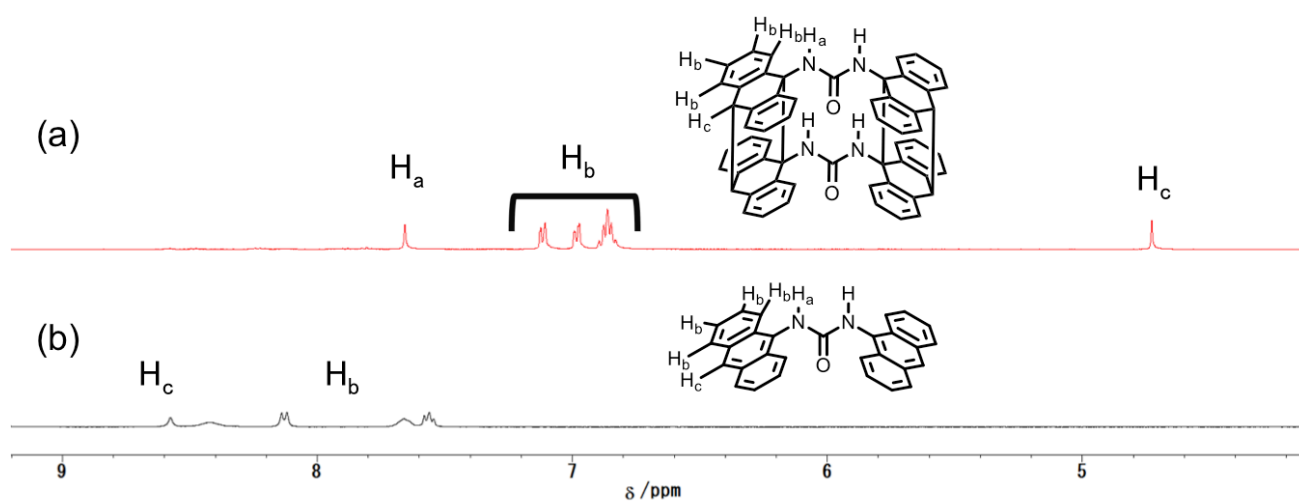


Figure S6.  $^1\text{H}$  NMR spectra of 9DAU (a) after 150 min and (b) before photoirradiation at 365 nm, respectively, in  $\text{DMSO-}d_6$ .

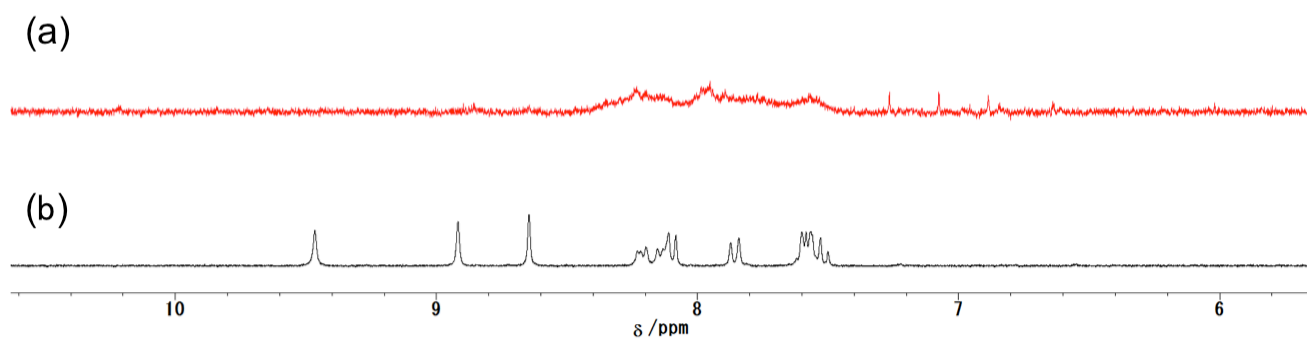


Figure S7. <sup>1</sup>H NMR spectra of 1DAU (a) after 360 min and (b) before photoirradiation at 365 nm, respectively, in DMSO-*d*<sub>6</sub>.



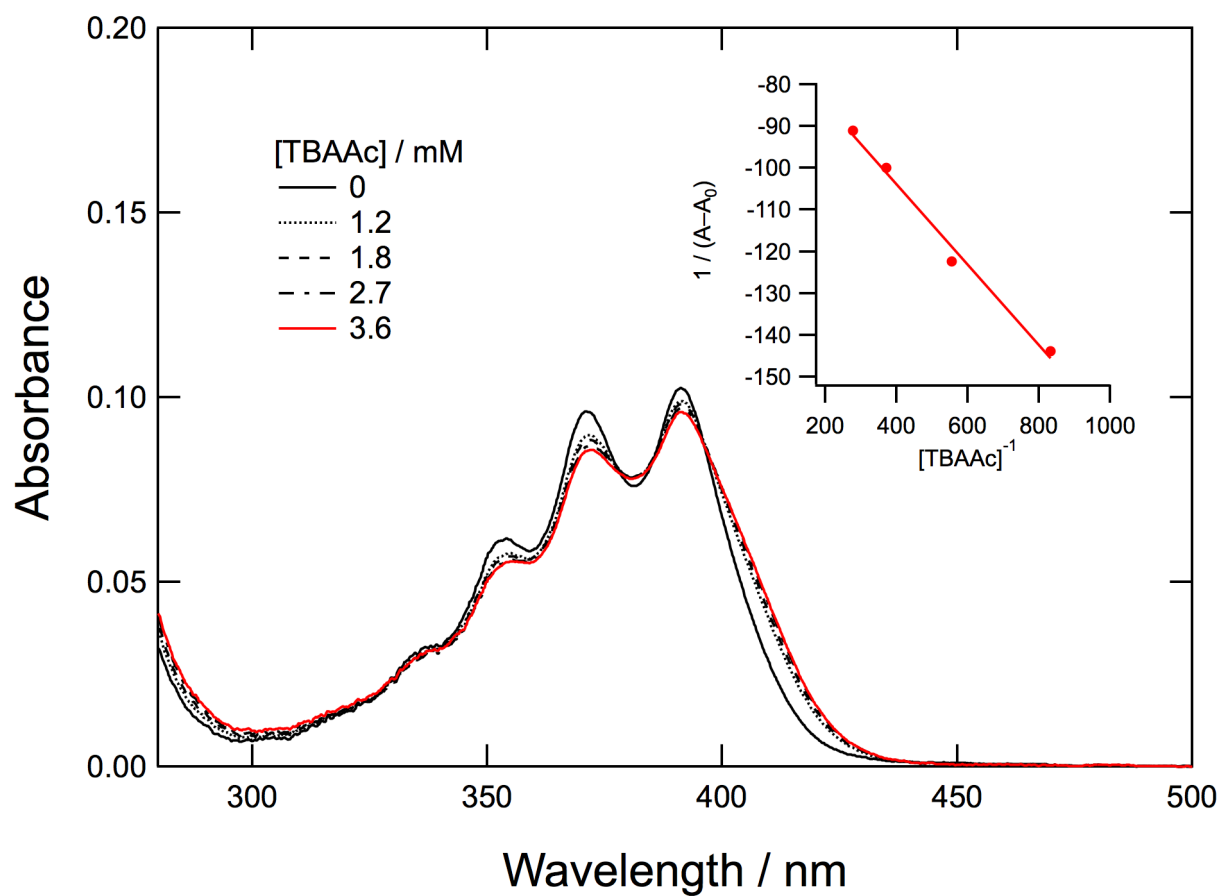


Figure S8. Changes in the absorption spectra of 9DAU in the presence of TBAAc and theoretical fit (solid line) of Eq. 2 to  $1/(A-A_0)$  against  $[TBAAc]^{-1}$ .

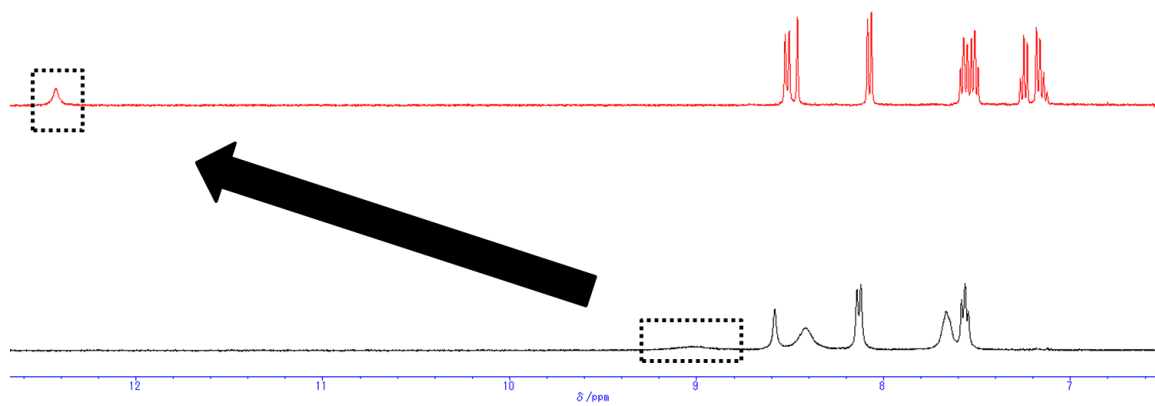


Figure S9. <sup>1</sup>H NMR spectra of 9DAU in the presence (top) and absence (bottom) of TBAAC in DMSO-*d*<sub>6</sub>.

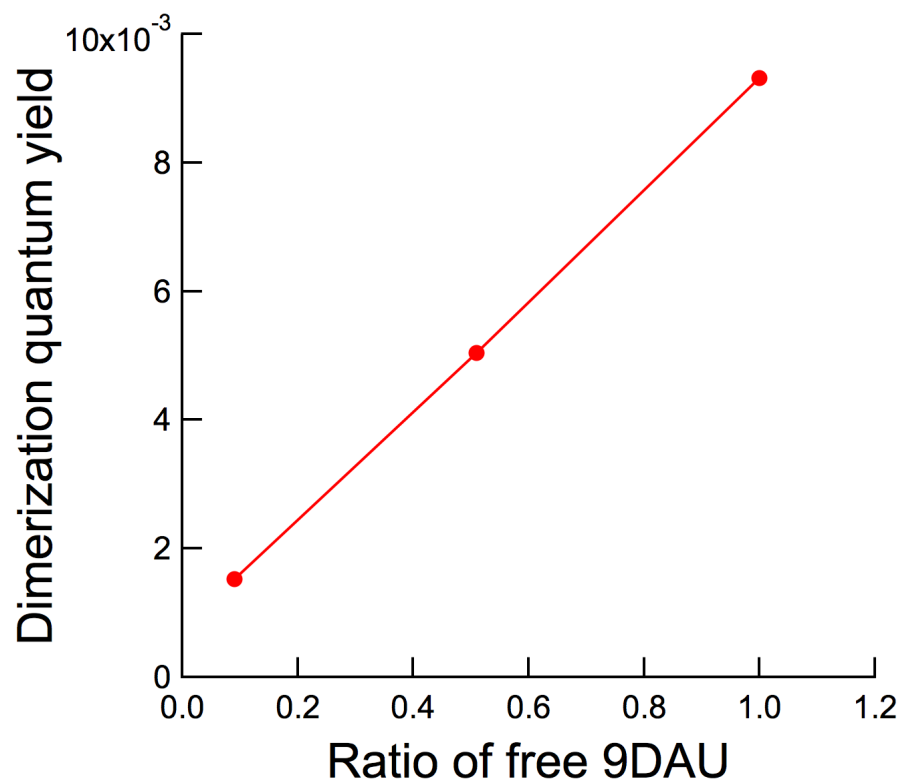


Figure S10. Plot of dimerization quantum yield against the ratio of free 9DAU along with linear regression.

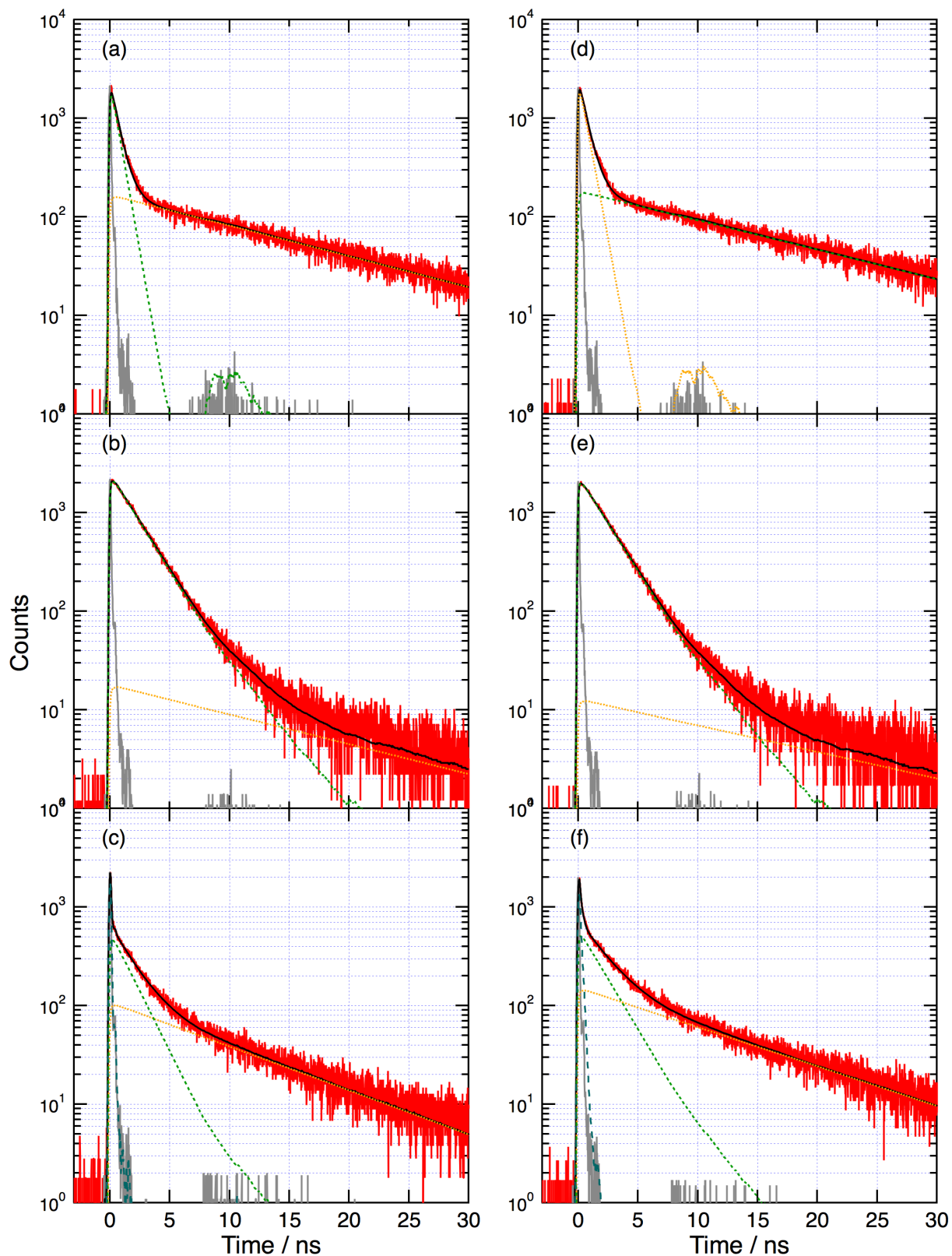


Figure S11. Fluorescence decay analyses of (a)(d) 1DAU, (b)(e) 2DAU and (c)(f) 9DAU monitored at (a)(b)(c) 450 nm and (d)(e)(f) 560 nm.

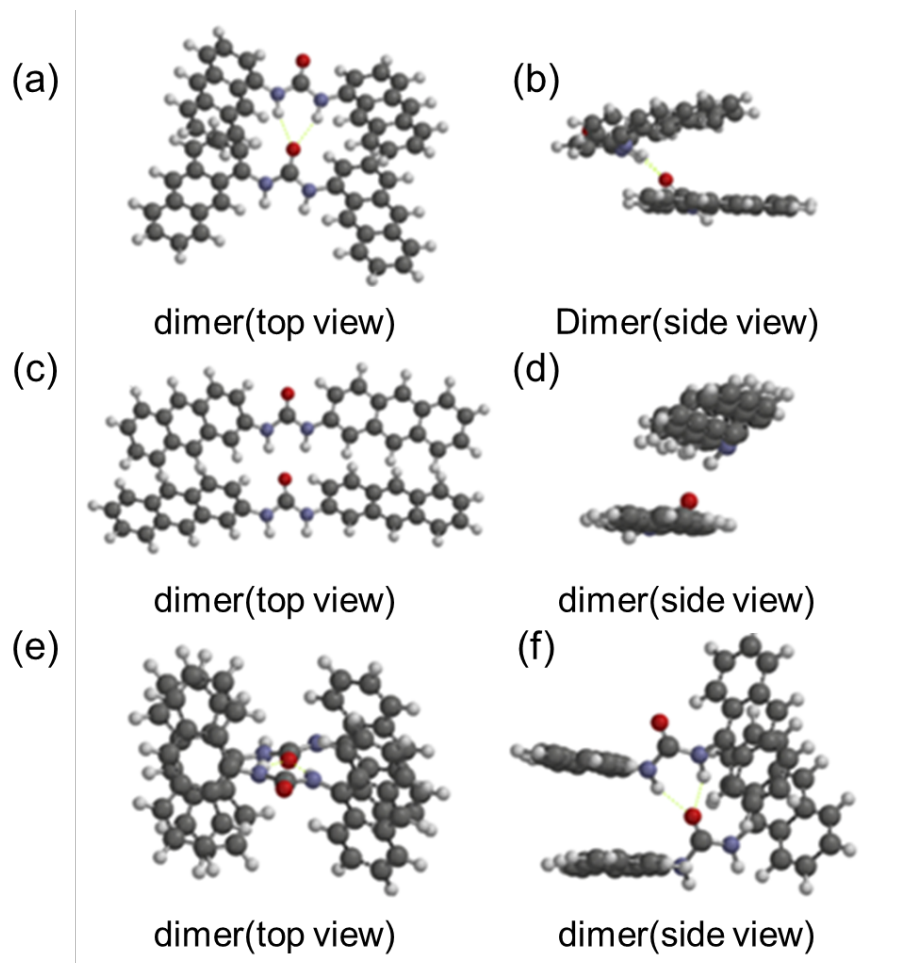


Figure S12. Dimer conformation of 1DAU, 2DAU and 9DAU by DFT calculation (B3LYP/ 6-31G\*).