SUPPORTING INFORMATION

Synthesis and Properties of Novel Fluorescent Switches

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General. All melting points are uncorrected. All commercially available materials were used without further purification. THF was distilled from Na / benzophenone before use. Toluene was distilled from CaH_2. Triethylamine was dried over KOH for several days and distilled. Dichloromethane was distilled from P_2O_5. Spectroscopic grade hexane was degassed using freeze-pump-thaw method for the photoirradiation experiments. Preparative TLC plates were prepared from neutral alumina (50-200 μm, standard activity I) and silica gel (60Å, 32-63 μm, standard grade) purchased from Sorbent Technologies. Photoirradiation was carried out using a standard UV lamp used for visualizing TLC plates and a 300 W halogen lamp as the light sources. All NMR spectra were recorded at 300 Hz. NMR chemical shifts are expressed in ppm relative to internal solvent peaks, coupling constants were measured in hertz. Fluorescence emission spectra were obtained with a single photon counting spectrofluorimeter. High resolution mass spectra were measured at Mass Spectrometry Laboratory in the University of Illinois at Urbana-Champaign (Q-Tof Ultima mass spectrometer was purchased in part with a grant from the National Science Foundation, Division of Biological Infrastructure (DBI-0100085)).

4,4-Difluoro-8-(4'-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (iodo-BODIPY). To a deoxygenated solution of 4-iodobenzaldehyde (1.22 g, 5.26 mmol) and 2,4-dimethylpyrrol (1g, 10.5 mmol) in dichloromethane (500 ml) several drops of trifluoroacetic acid were added and the mixture was stirred overnight. After the addition of *p*-chloranil (1.98 g, 8 mmol), the reaction mixture was stirred 30 min, after which $BF_3(C_2H_5O)_2$ (5 ml, 41mmol) and Et_3N (8 ml, 57 mmol) were added at 0 ºC. After additional stirring for 40 min at r.t., the solution was washed with $NaHCO_3$ and water. Collected organic phases were dried over $MgSO_4$, concentrated and filtered through a shot plug of silica gel. After removal of the solvent, the residue was purified by silica gel preparative TLC using a mixture of hexane and dichloromethane (1 : 1 v/v) to yield the product as a red-orange solid (24 mg, 53 µmol, 10%). mp = 213-215 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.42, (s, 6H), 2.55 (s, 6H), 5.99 (s, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H); MS (EI) *m/z* = 450 (M^+).

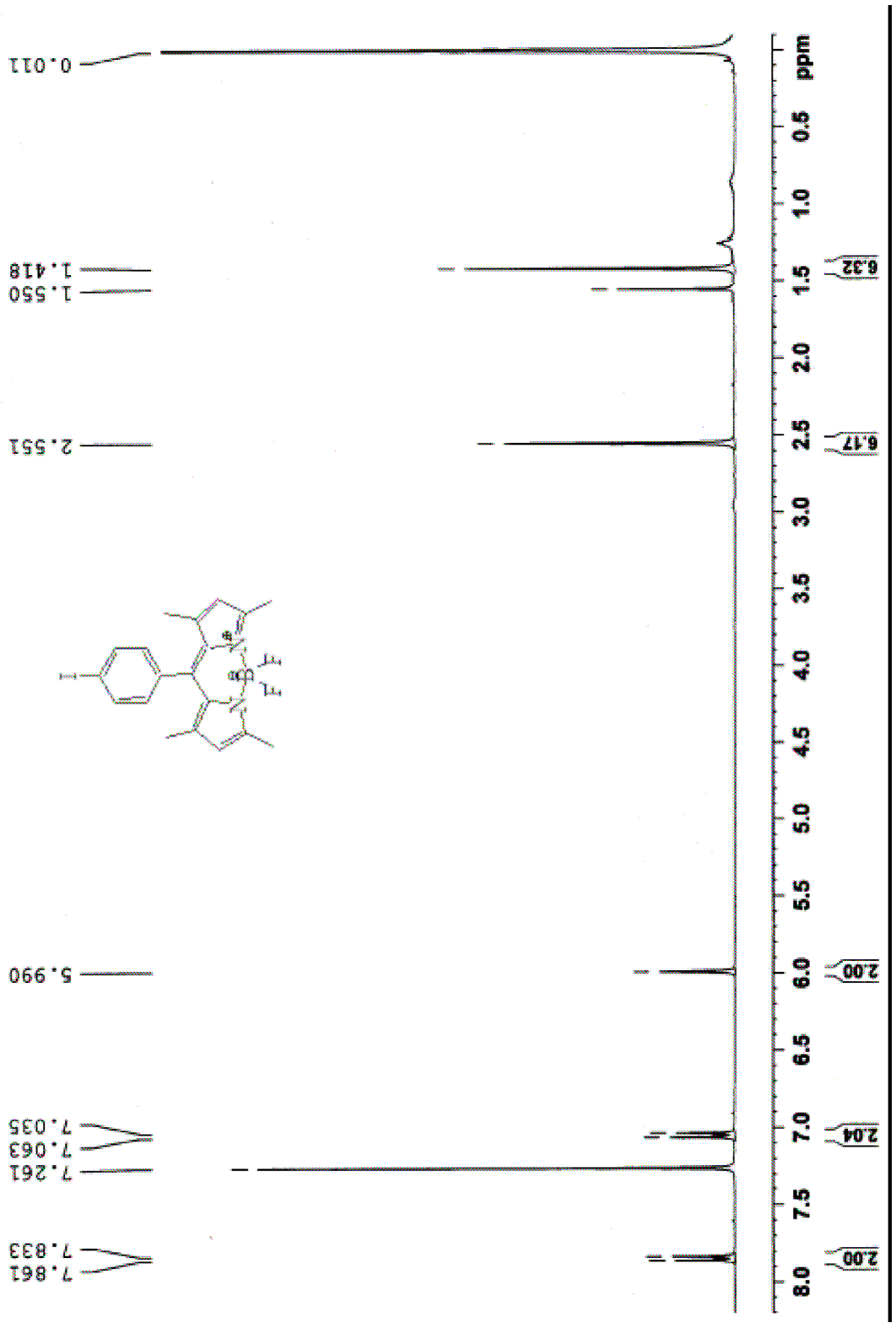

Figure S1. ^{1}H NMR spectrum of iodo-BODIPY in $CDCl_3$

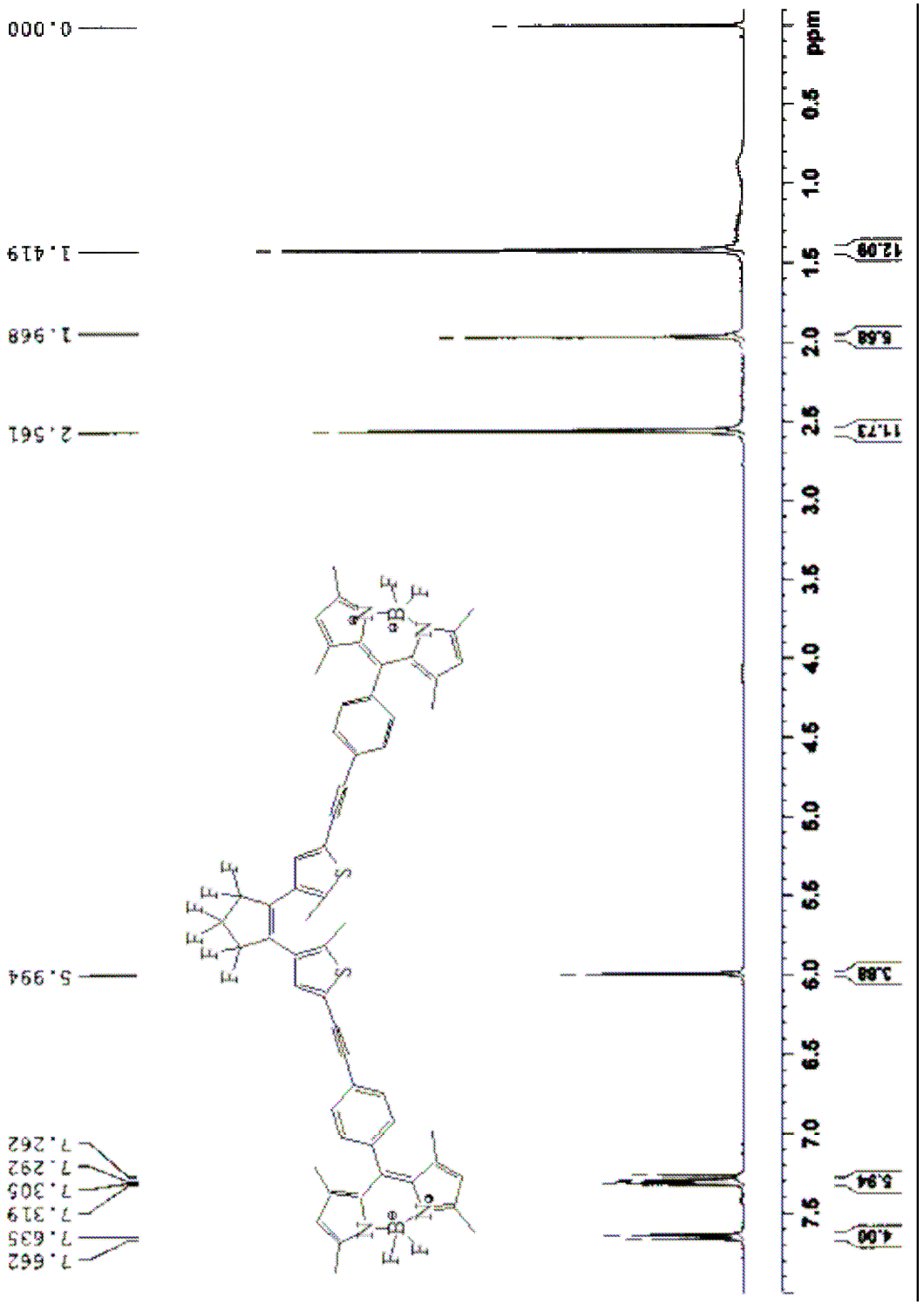

Figure S2. ^{1}H NMR spectrum of **1** in $CDCl_3$

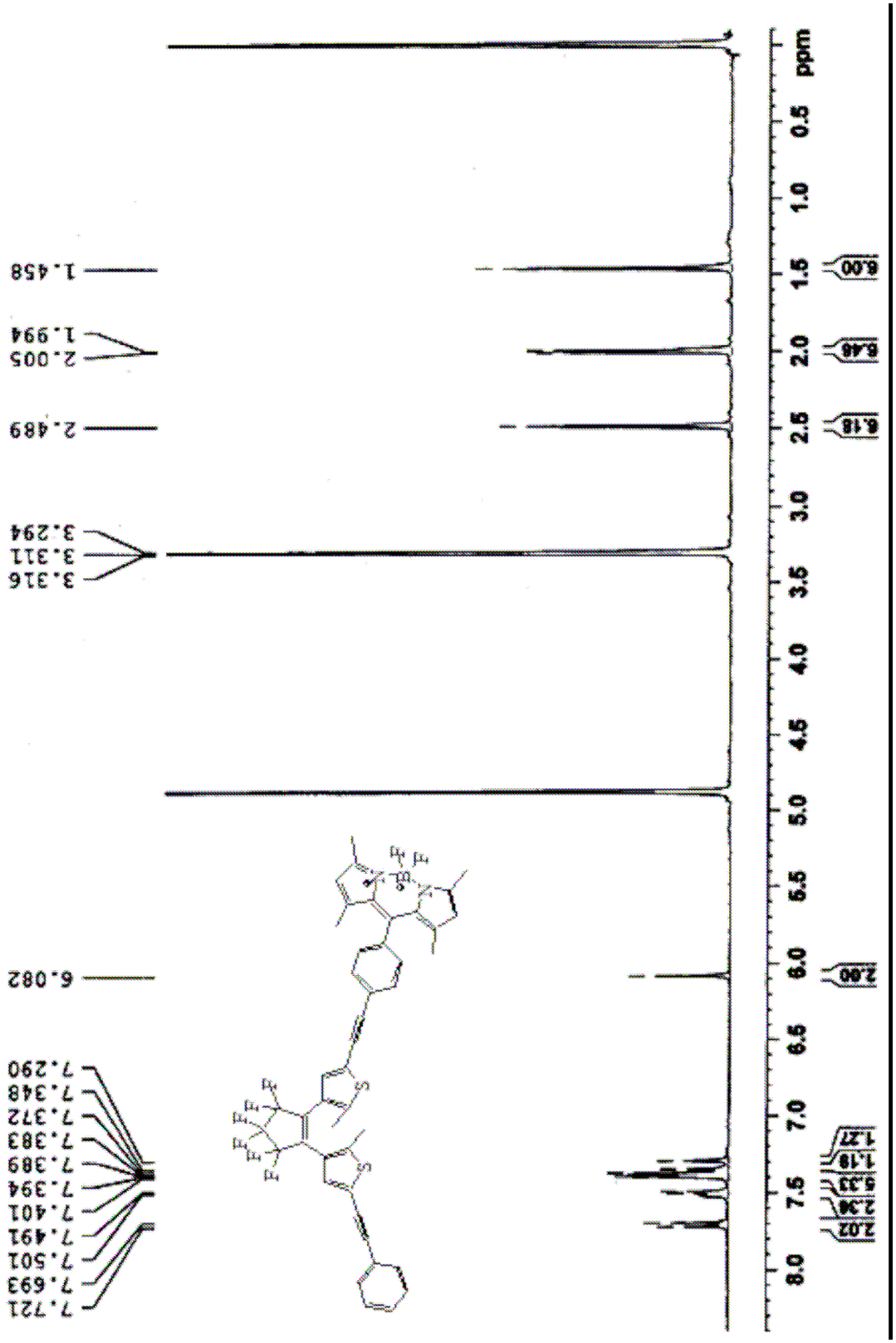

Figure S3. ^{1}H NMR spectrum of **2** in MeOD

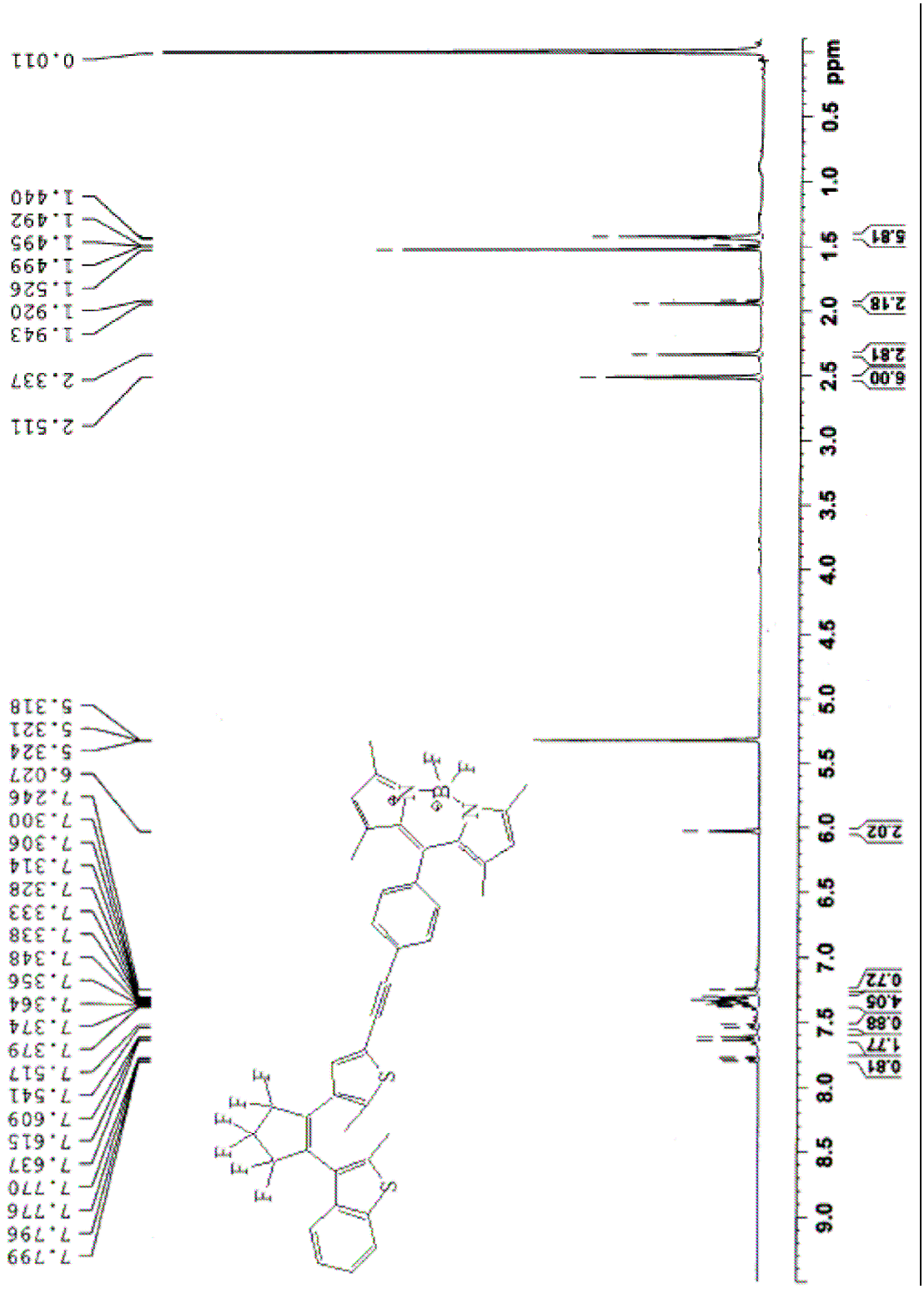

Figure S4. ^{1}H NMR spectrum of **3** in CD_2Cl_2

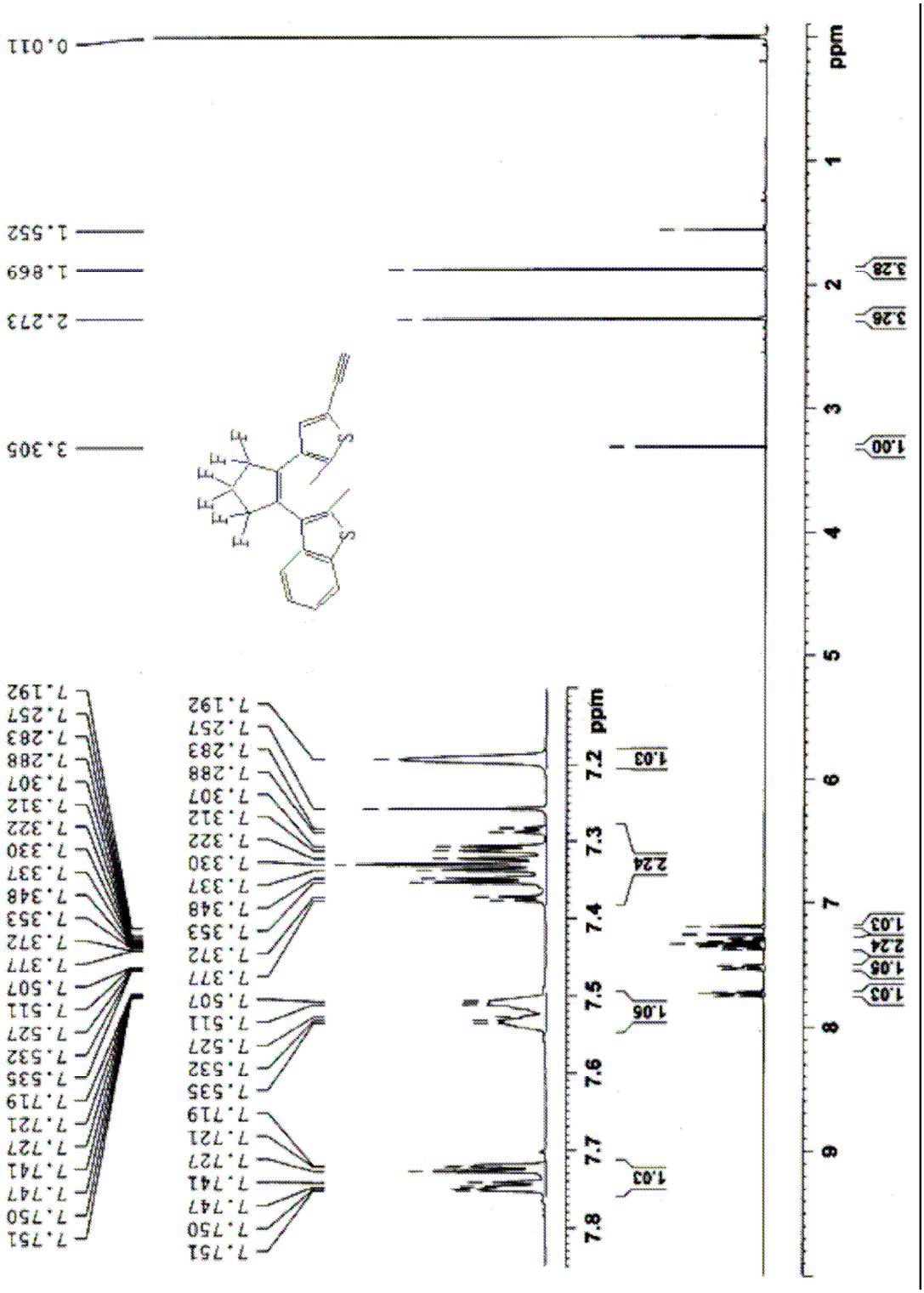

Figure S5. ^{1}H NMR spectrum of **5**

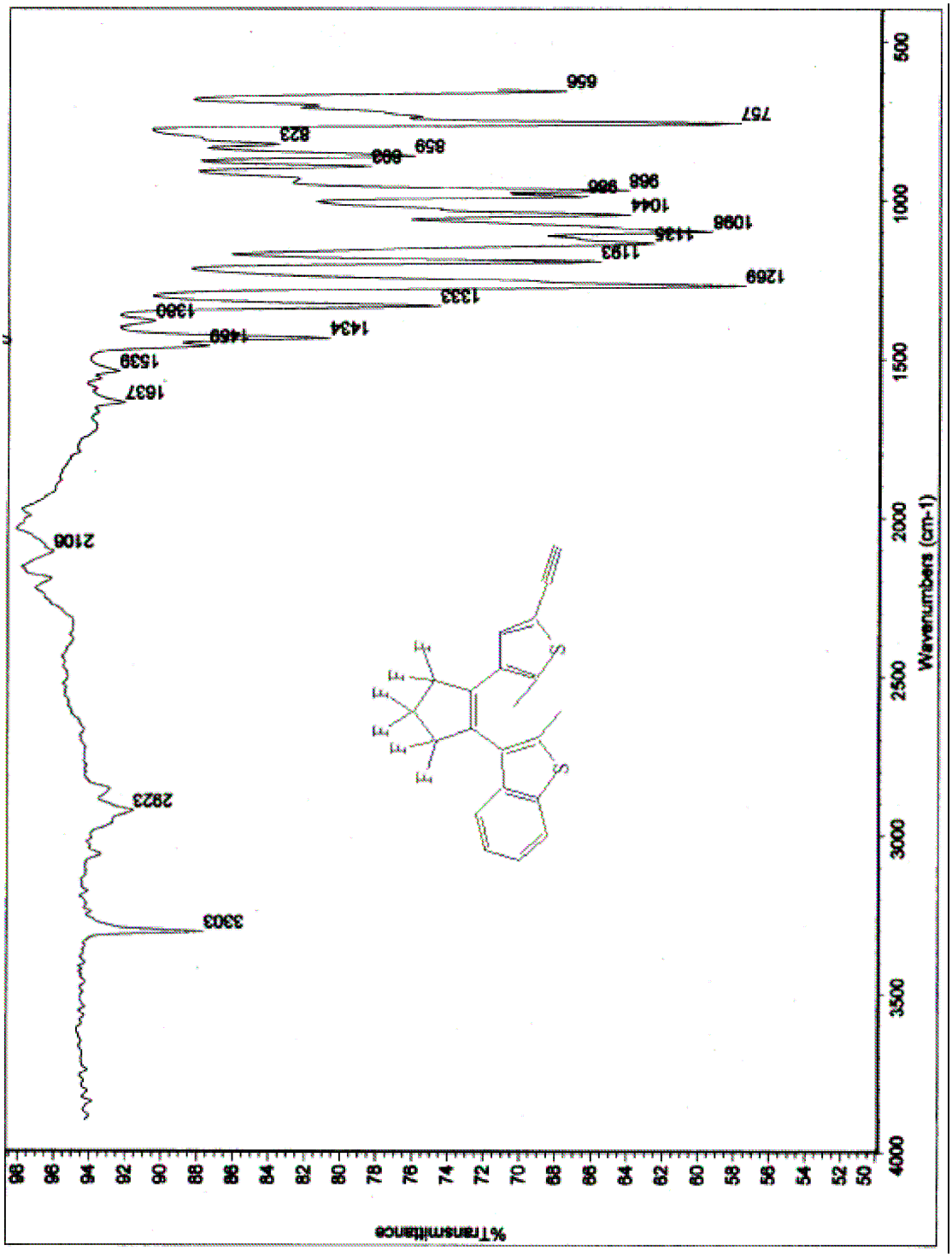

Figure S6. Solid state IR spectrum of **5**

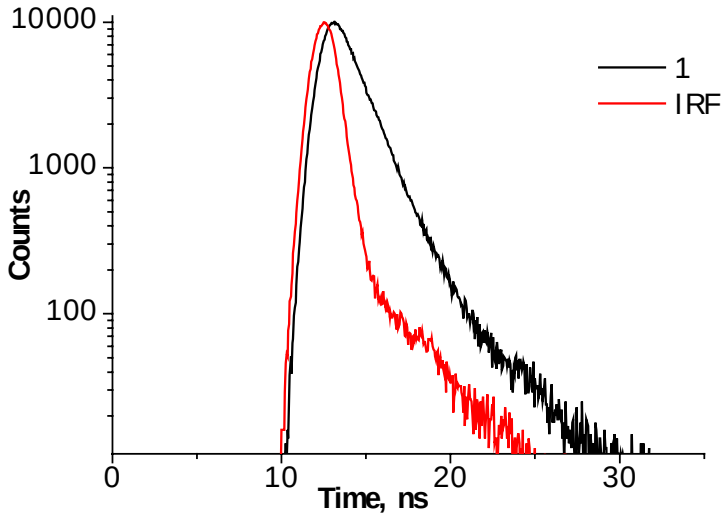

Figure S7. Fluorescence decay curve for **1.**

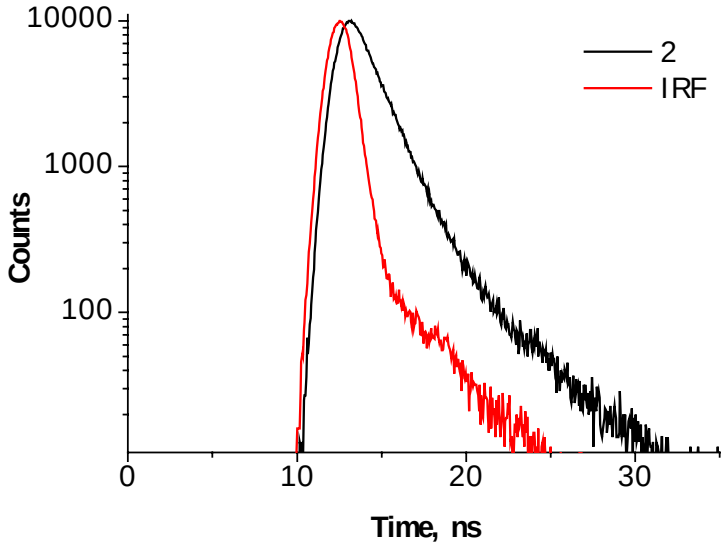

Figure S8. Fluorescence decay curve for **2.**

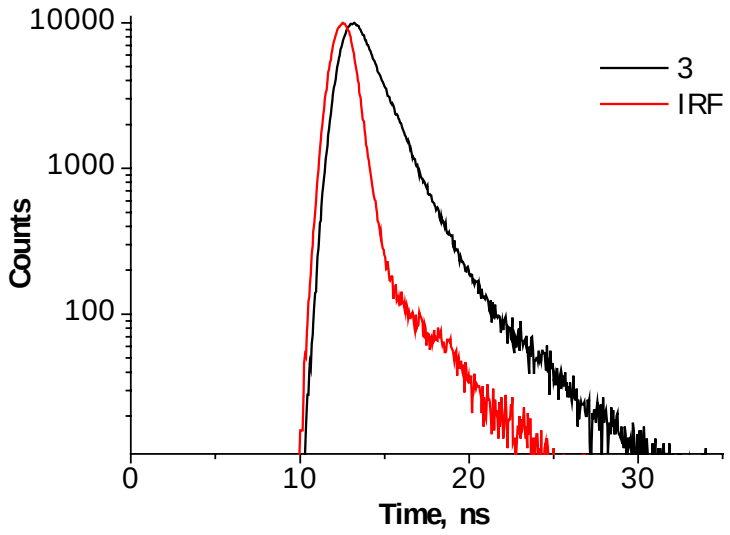

Figure S9. Fluorescence decay curve for **3.**

Procedure for Irradiation Experiments

A standard UV lamp used for visualizing TLC plates was used to carry out the ring-closing reaction (λ = 254 nm). The ring-opening reaction was carried out using the light of a 300 W halogen lamp as a light source. The hexane solutions of **1** – **3** were degassed using freeze-pump-thaw method. Irradiation times were 1 min for both ring-closing and ring-opening reactions.

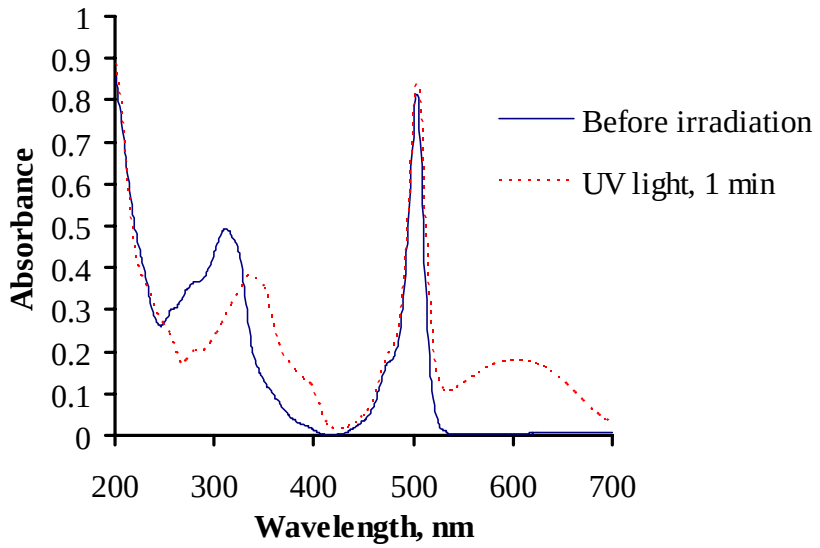

Figure S10. Absorption spectral changes of **2** (7.9×10^{-6} M in hexane) before (solid line) and after (dotted line) irradiation with UV light.

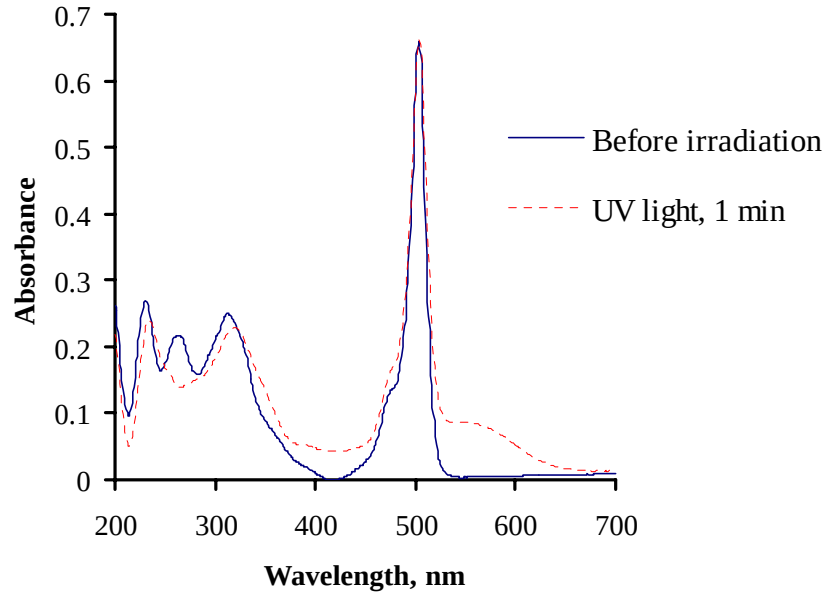

Figure S11. Absorption spectral changes of **3** (7.4×10^{-6} M in hexane) before (solid line) and after (dotted line) irradiation with UV light.

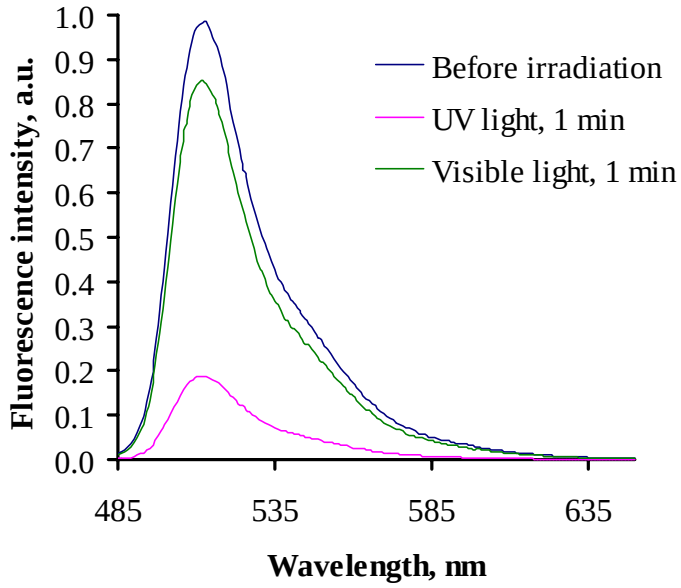

Figure S12. Fluorescence spectra of **2** (4.1×10^{-6} M in hexane, λ_{exc} = 480 nm) before irradiation, at photostationary state after UV light irradiation and after visible light irradiation.

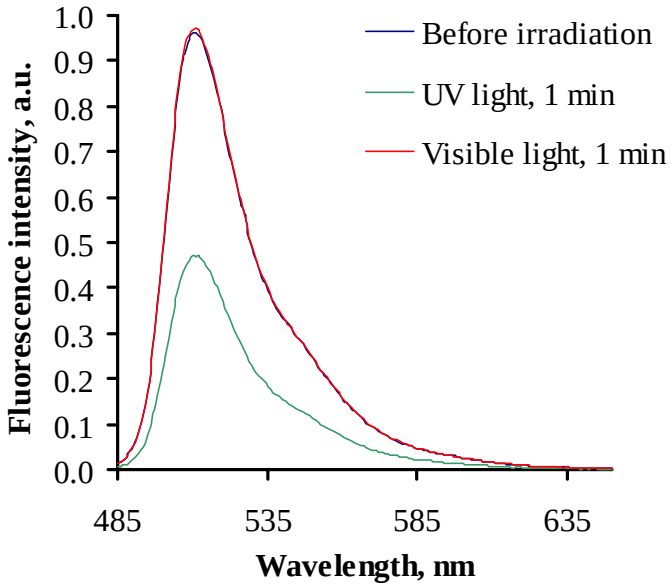

Figure S13. Fluorescence spectra of **3** (4.7×10^{-6} M in hexane, λ_{exc} = 480 nm) before irradiation, at photostationary state after UV light irradiation and after visible light irradiation.

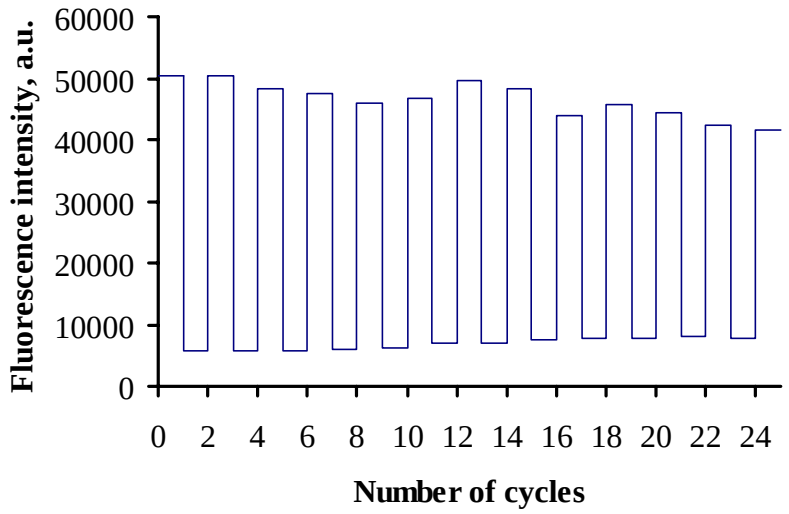

Figure S14. Multiple quenching and recovery of fluorescence of **1** (3.0×10^{-6} M in hexane, λ_{exc} = 480 nm). Number of cycles is 24.

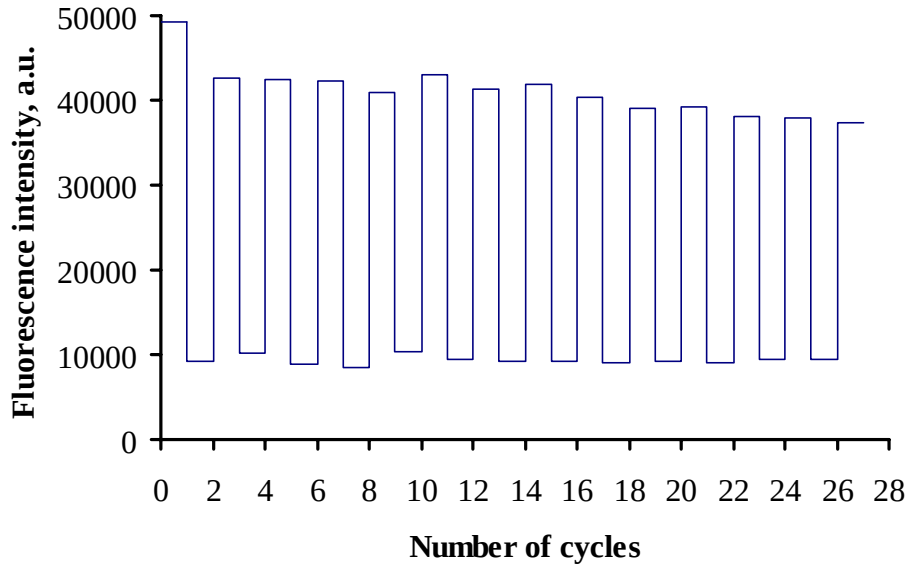

Figure S15. Multiple quenching and recovery of fluorescence of **2** (4.1×10^{-6} M in hexane, λ_{exc} = 480 nm). Number of cycles is 26.

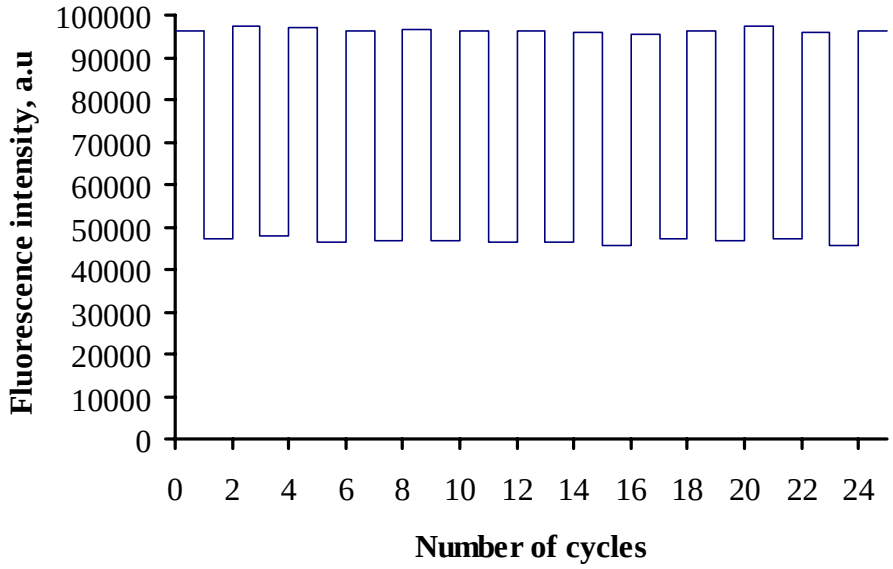

Figure S16. Multiple quenching and recovery of fluorescence of **3** (4.7×10^{-6} M in hexane, λ_{exc} = 480 nm). Number of cycles is 24.

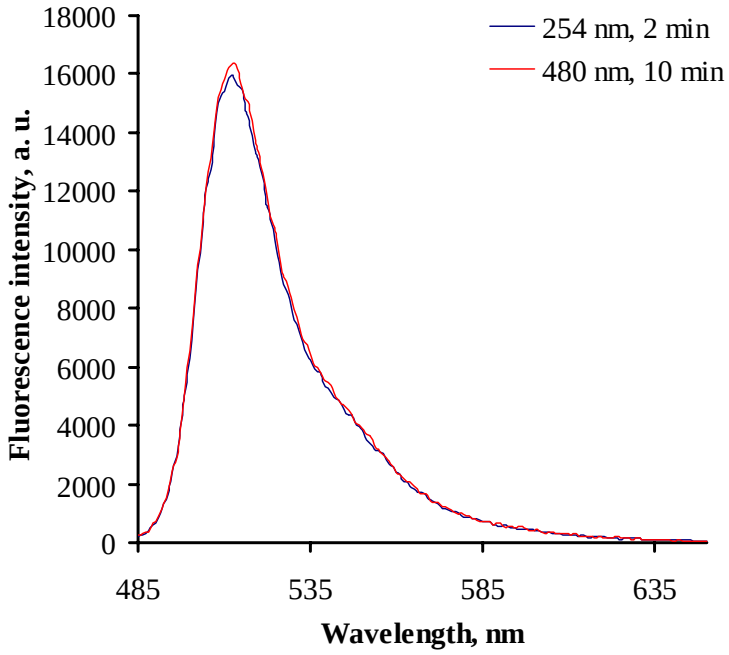

Figure S17. Fluorescence emission spectra of **2** (7.9×10^{-6} M in hexane, λ_{exc} = 480 nm) after 254 nm and 480 nm light irradiations during 2 min and 10 min, respectively.