Electronic Supplementary Information

Optical Writing and Reading with a Photoactivatable Carbazole

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Experimental Procedures

Synthesis. Chemicals were purchased from commercial sources and used as received with the exception of MeCN, which was distilled over CaH_2. Compounds **3** and **4** were prepared according to literature procedures.[S1,S2] ESIMS were recorded with a Bruker micrOTO-Q II spectrometer. NMR spectra were recorded with a Bruker Avance 400 spectrometer.

1. A solution of **3** (80 mg, 0.38 mmol), **4** (100 mg, 0.32 mmol) and TFA (20 µL, 0.26 mmol) in MeCN (20 mL) was heated under reflux for 18 hours. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in CH_2Cl_2 (5 mL). The addition of hexane (10 mL) caused the formation of a dark red precipitate. The suspension was cooled down to 0 ºC and the precipitate was filtered off. The resulting solid was dissolved in CH_2Cl_2 (30 mL) and washed with a saturated aqueous solution of K_2CO_3 (3 × 100 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was distilled off under reduced pressure to afford **1** (15 mg, 0.03 mmol, 9%) as a dark red solid. ESIMS: *m/z* = 502.2148 $[M + H]^+$ (*m/z* calcd. for $C_{32}H_{28}N_3O_3$ = 502.2131); ^1H NMR (CD_3CN): δ = 8.23 (1H, s, ^{ar}H), 8.09 (1H, d, ^{ar}H, 8 Hz), 7.60–7.17 (9H, m, ^{ar}H), 7.06 (1H, m, ^{ar}H), 7.03 (1H, d, =C*H*, 16 Hz), 6.83 (1H, m, ^{ar}H), 6.73 (1H, d, ^{ar}H, 8 Hz), 6.50 (1H, d, =C*H*, 16 Hz), 5.04 (1H, d, CH_2, 19 Hz), 4.86 (1H, d, CH_2, 19 Hz), 3.81 (3H, s, N–CH_3), 1.56 (3H, s, CH_3), 1.23 (3H, s, CH_3) ppm.

2. A solution of **3** (1 g, 4.78 mmol), **5** (800 mg, 5.02 mmol) and TFA (20 µL, 0.26 mmol) in EtOH (20 mL) was heated under reflux for 18 hours. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2: hexane:CH_2Cl_2 (7:3 v/v) → CH_2Cl_2/AcOEt (7:3 v/v)] and crystallized from hexane to give **2** (450 mg, 1.28 mmol, 27%) as a yellow solid. ESIMS: *m/z* = 351.1875 $[M + H]^+$ (*m/z* calcd. for $C_{25}H_{23}N_2$ = 351.1861); ^1H NMR [$(CD_3)_2CO$] δ = 8.58 (1H, d, ^{ar}H, 2 Hz), 8.22 (1H, d, ^{ar}H, 8 Hz), 8.03 (1H, d, =C*H*, 16 Hz), 7.92 (1H, dd, ^{ar}H, 2 and 8 Hz), 7.61 (1H, d, ^{ar}H, 8 Hz), 7.58 (1H, d, ^{ar}H, 8 Hz), 7.53 (1H, d, ^{ar}H, 8 Hz), 7.51 (1H, ddd, ^{ar}H, 1, 8 and 8 Hz), 7.43 (1H, d, ^{ar}H, 8 Hz), 7.32 (1H, ddd, ^{ar}H, 1, 8 and 8 Hz), 7.30 (1H, d, =C*H*, 16 Hz), 7.27 (1H, ddd, ^{ar}H, 1, 8 and 8 Hz), 7.21 (1H, ddd, ^{ar}H, 1, 8 and 8 Hz), 3.95 (3H, s, N–CH_3), 1.50 (6H, s, 2 × CH_3) ppm.

Absorption and Emission Spectroscopies. Absorption spectra were recorded with a Varian Cary 100 Bio spectrometer, using quartz cells with a path length of 1.0 cm. Emission spectra were recorded with a Varian Cary Eclipse spectrometer in aerated solutions. Fluorescence quantum yields were determined with a 9,10-diphenylanthracene standard, following a literature protocol.[S3] Samples were illuminated with a Luzchem Research LZC-4V photoreactor (350 nm, 4.88 mW cm^{-2}) for the experiments in Figures 2 and 3. Fluorescence decays (Table S1 and Fig. S7–S12) were recorded with a PicoQuant Fluotime 200 time-correlated single photon counting system, using pulsed laser excitation at 375 nm and a Picoquant's PMA 182-M single photon detector. The excitation laser worked at 10 MHz repetition rate and the photon counting frequency was kept always below 1%. Time-resolved emission signals were analyzed by fitting the convolution of the instrument's response function with a multiexponential decay model using the PicoQuant FluoFit 4.0 software. The time resolution of the system is approximately 100 ps. The number of exponentials in the model function and the corresponding goodness of the fit was judged by the distribution of residuals and the value of the Chi-square parameter.

[S1] M. Grigoras and N.-C. Antonoaia, *Eur. Polym. J.*, 2005, **41**, 1079–1089.

[S2] Y. Zhang, S. Swaminathan, S. Tang, J. Garcia-Amorós, M. Boulina, B. Captain, J. D. Baker, F. M. Raymo, *J. Am. Chem. Soc.*, **2015**, *137*, DOI:10.1021/ja5125308.

[S3] J. Stampfl, S. Tasch, G. Leising and U. Scherf, *Synt. Met.*, 1995, **71**, 2125−2128.

Square Wave Voltammetry. Voltammograms were recorded with a CH Instruments 610A electrochemical analyzer in MeCN under Ar, using a three-electrode cell. The reference was a Ag/Ag$^+$ electrode (1 mM $AgNO_3$ in MeCN). The counter and working were a platinum wire and a glassy-carbon electrode respectively. The supporting electrolyte was Bu_4NPF_6 (50 mM). The scan rate was 50 mV s^{-1}.

Silver Nanoparticles. Aqueous NaOH (1.2 M, 0.1 mL) was added to aqueous $AgNO_3$ (0.22 g, 26 mL) under vigorous stirring. A dark-brown precipitate formed immediately. Aqueous NH_4OH (7.3 M, 1 mL) was added dropwise to dissolve the precipitate. The resulting clear solution was cooled down to 5 °C. Glass slides were submerged in the cooled solution and aqueous D-glucose (0.35 g, 4 mL) was added. The mixture was stirred for 2 min at 5 °C, allowed to warm up to ambient temperature, heated to 40 °C and stirred for a further 10 min at this temperature. In the process, the yellow-green solution turned brown and a greenish coating deposited on the slides. The slides were removed from the solution, washed with H_2O, sonicated in H_2O for 1 min at ambient temperature, washed again with H_2O and dried in air for 2 hours.

Atomic Force Microscopy. Atomic force microscopy (AFM) measurements were performed with a Multimode 8 system attached to a Bruker Nanoscope V electronics unit. Topographic data were acquired in Asyst Mode and Set point (proportional to the force exerted by the probe on the sample) was kept in automatic mode. All samples were analyzed using silicon nitride triangular levers with silicon oxide pyramidal tips (Bruker SNL-10, nominal spring constant = 0.35 nN·nm^{-1}). Samples were glued to metallic discs with a two-component epoxy cement (Pattex Natural 27) and stored for 1 hour in air before the experiments. Images were captured at 20 × 20, 10 × 10, 2 × 2 and 1 × 1 μm to characterize each sample at different scales. The resolution was set to 512 × 512 pixels and the scan rate was adjusted between 0.1 and 0.5 Hz to optimize the images. The recorded data were analyzed with Bruker Nanoscope Analysis software.

Polymer Films. A solution of PBMA (10 mg mL^{-1}, $M_W = 337 \times 10^3$) and either **1** or **2** (3% w/w relative to PBMA) was deposited dropwise on either a glass or a quartz slide. The substrate was spun at 1500 rpm for 3 min with a Chemat Technologies KW-4A spin coater. The coated slides were stored under reduced pressure for 6 hours prior to any imaging and spectroscopic experiments. The same protocol was employed to deposit polymer films on glass slides pre-coated with silver nanoparticles. The thickness (*ca.* 0.2 μm) of the resulting films was measured with a Veeco Dektak Mechanical Profilometer. Fluorescence images of the substrates were recorded with a Leica SP5 confocal laser-scanning microscope.

Table S1. Fluorescence decay times for **1** after irradiation (λ_{Ac} = 350 nm, 4.88 mW cm^{-2}, 10 min) and for **2** in MeCN solution and PBMA films (3% w/w) without and with silver nanoparticles. The values in parenthesis indicate the fractional amplitudes of the different positive decay components.

		τ_1 (ns)	τ_2 (ns)
1	MeCN	0.65 (76%)	3.6 (24%)
	PBMA	0.13 (90%)	1.1 (10%)
	PBMA + AgNPs	0.10 (94%)	0.78 (6%)
2	MeCN	0.94 (66%)	3.8 (34%)
	PBMA	0.15 (87%)	1.1 (13%)
	PBMA + AgNPs	0.15 (86%)	0.79 (14%)

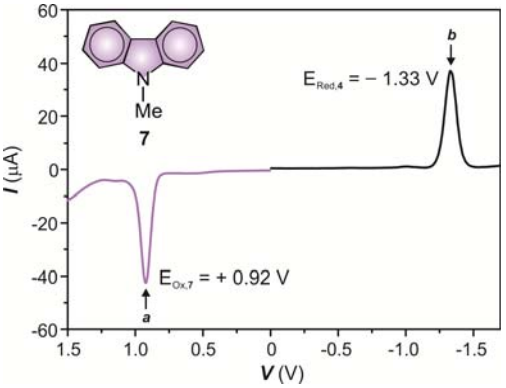

Fig. S1. Square wave voltammograms [50 mV s^{-1}, V *vs.* Ag/Ag^{+} (1 mM in AgNO$_3$, Bu$_4$NPF$_6$ (50 mM)] of MeCN solutions (100 µM, 20 ºC) of **7** (***a***) and **4** (***b***).

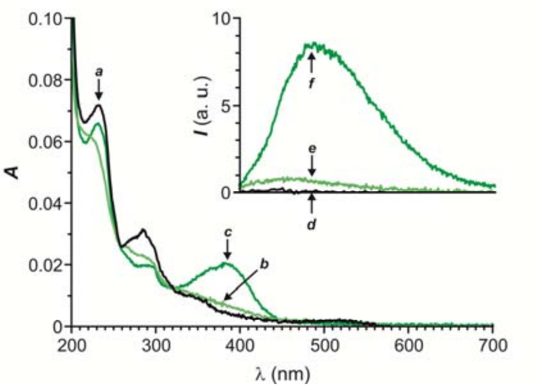

Fig. S2. Absorption (***a–c***) and emission (***d–f***, λ_{Ex} = 380 nm) spectra of PBMA films doped (3% w/w, 20 ºC) with either **1**, before (***a*** and ***d***) and after (***b*** and ***e***) irradiation (λ_{Ac} = 350 nm, 4.88 mW cm^{-2}, 10 min), or **2** (***c*** and ***f***) and deposited on quartz slides.

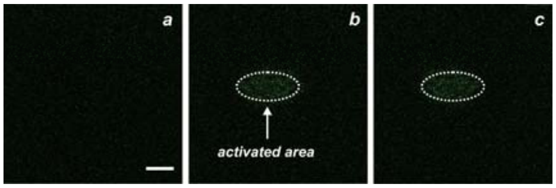

Fig. S3. Confocal laser-scanning fluorescence images (λ_{Ex} = 405 nm, λ_{Em} = 430–650 nm, scale bar = 30 µm) of a PBMA film, doped with **1** (3% w/w) and deposited on a glass slide, recorded before (***a***), immediately (***b***) and 10 min (***c***) after illumination (λ_{Ac} = 405 nm, 0.1 mW, 300 s) of an ellipsoidal area within the imaging field.

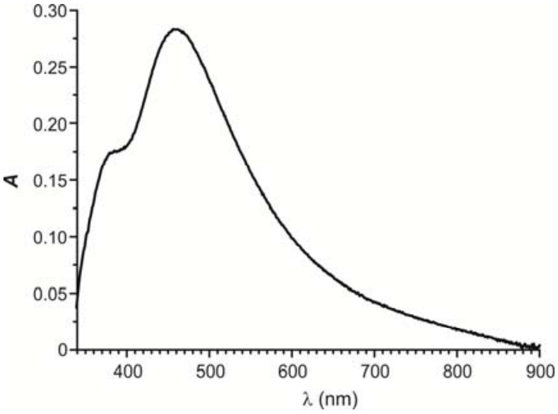

Fig. S4. Absorption spectrum of silver nanoparticles deposited on a quartz slide.

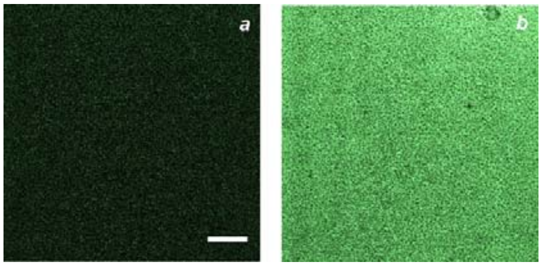

Fig. S5. Fluorescence images (λ_{Ex} = 405 nm, λ_{Em} = 450–650 nm, scale bar = 30 µm) of PBMA films doped with **2** (3% w/w) and deposited on glass slides without (***a***) and with (***b***) silver nanoparticles on their surface.

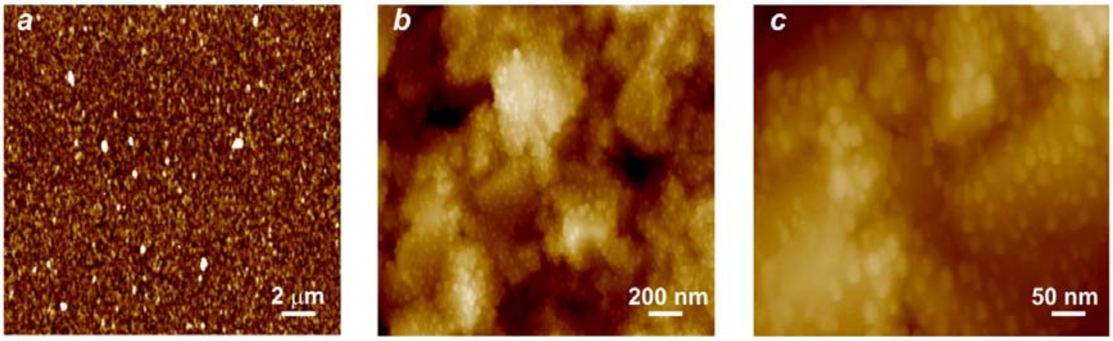

Fig. S6. AFM images of silver nanoparticles deposited on a glass slide captured at increasing magnification (***a*** → ***c***).

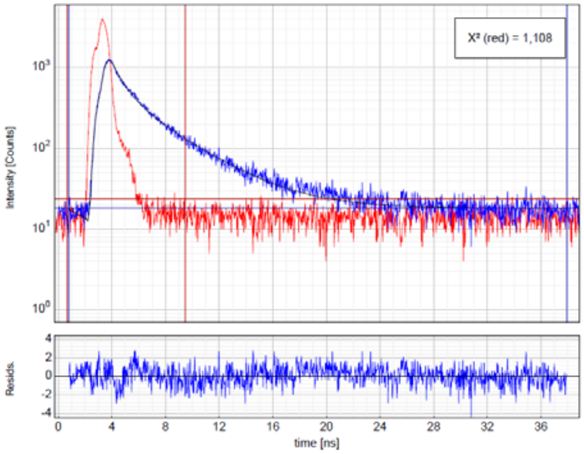

Fig. S7. Fluorescence decay (λ_{Ex} = 375 nm, λ_{Em} = 490 nm) of a MeCN solution (10 µM, 20 ºC) of **1** after irradiation (blue trace, λ_{Ac} = 350 nm, 4.88 mW cm^{-2}, 10 min), fitted function (black line) and instrument response function (red trace).

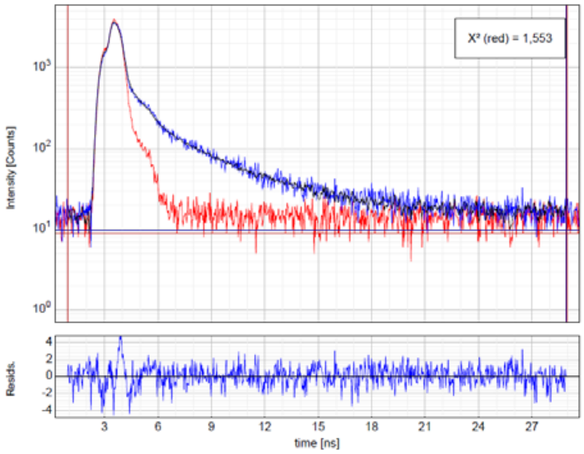

Fig. S8. Fluorescence decay (λ_{Ex} = 375 nm, λ_{Em} = 490 nm) of a MeCN solution (10 µM, 20 ºC) of **2** after irradiation (blue trace, λ_{Ac} = 350 nm, 4.88 mW cm^{-2}, 10 min), fitted function (black line) and instrument response function (red trace).

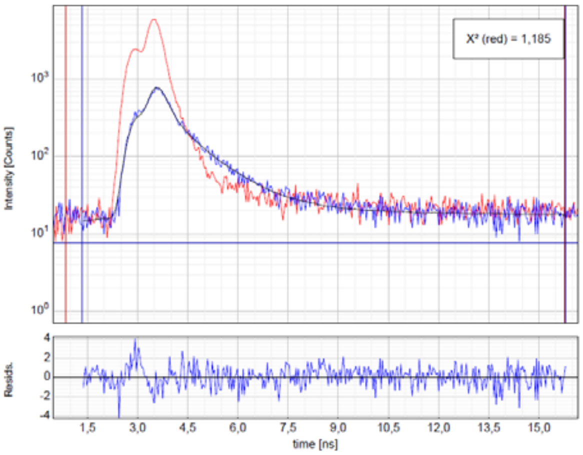

Fig. S9. Fluorescence decay ($\lambda_{Ex} = 375$ nm, $\lambda_{Em} = 490$ nm) of a PBMA film doped with **1** (3% w/w) after irradiation (blue trace, $\lambda_{Ac} = 350$ nm, 4.88 mW cm^{-2}, 10 min), fitted function (black line) and instrument response function (red trace).

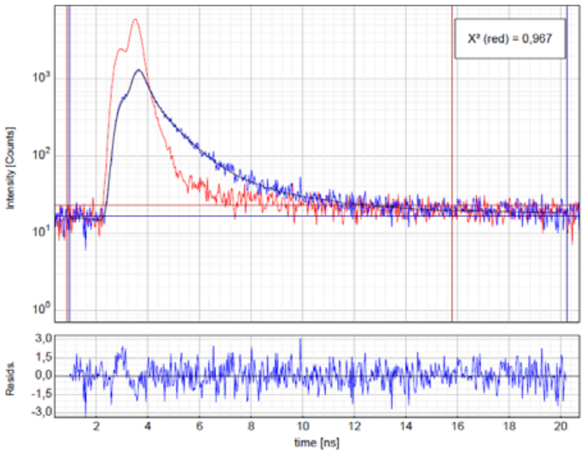

Fig. S10. Fluorescence decay ($\lambda_{Ex} = 375$ nm, $\lambda_{Em} = 490$ nm) of a PBMA film doped with **2** (3% w/w) after irradiation (blue trace, $\lambda_{Ac} = 350$ nm, 4.88 mW cm^{-2}, 10 min), fitted function (black line) and instrument response function (red trace).

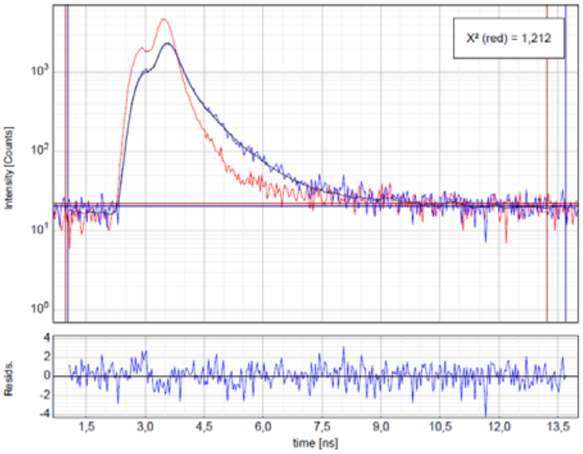

Fig. S11. Fluorescence decay ($\lambda_{Ex} = 375$ nm, $\lambda_{Em} = 490$ nm) of a PBMA film doped with **1** (3% w/w) and deposited on a glass slide with silver nanoparticles on its surface, after irradiation (blue trace, $\lambda_{Ac} = 350$ nm, 4.88 mW cm^{-2}, 10 min), fitted function (black line) and instrument response function (red trace).

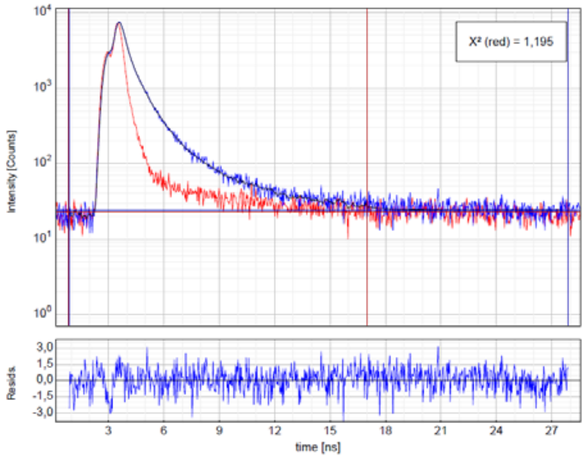

Fig. S12. Fluorescence decay ($\lambda_{Ex} = 375$ nm, $\lambda_{Em} = 490$ nm) of a PBMA film doped with **2** (3% w/w) and deposited on a glass slide with silver nanoparticles on its surface, after irradiation (blue trace, $\lambda_{Ac} = 350$ nm, 4.88 mW cm^{-2}, 10 min), fitted function (black line) and instrument response function (red trace).