

Supporting Information

Intragel Photoreduction of Aryl Halides by Green-to-Blue Upconversion under Aerobic Conditions

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1. Materials

1.1. Chemicals: All reagents and solvents were used as received unless otherwise indicated. Platinum(II) octaethylporphyrin (**PtOEP**), 9,10-diphenylanthracene (**DPA**), 4-bromoacetophenone, 2-bromoacetophenone, 4-bromobenzonitrile, 3-bromoquinoline, 4-iodoacetophenone, and acetophenone were commercially available. *N,N*-Dimethylformamide (DMF, p.a. grade) was used as solvent without further purification. Anhydrous DMF (Aldrich) was used for experiments under nitrogen atmosphere. LMW gelators **G-1**¹ and **G-2**² were synthesized according to literature procedures and showed spectroscopic data in agreement to those published.

1.2. Organogels: Doped organogels were prepared in clear glass vials (2 mm in diameter × 4 mm in height) by the following general procedure: A suspension of **G-1** (10 g L⁻¹), **1** (10 mM), **PtOEP** (33 μM), **DPA** (6.7 mM) and *n*-pentadecane (10 mM, internal standard) in DMF (2 mL) was gently heated with a heat gun at 80 °C during 1 min until an isotropic solution was obtained. The corresponding gel was obtained upon cooling the mixture to RT. The so-obtained phase was preliminary classified as “gel” if it did not exhibit gravitational flow upon turning the vial upside-down. The viscoelastic nature of the material was further confirmed by oscillatory rheological measurements.

Notes: (1) No control over the temperature rate was applied during the heating-cooling process. (2) Flame-dried glassware, anhydrous solvents and nitrogen-purged chemicals were employed for the preparation of the gel under nitrogen atmosphere, which was also maintained during the irradiation process.

2. Methods

2.1. T_{gel} determination: Gel-to-sol transition temperatures were determined using a custom made set-up where a sealed vial was placed into a mold of an alumina block and heated up at 1 °C/5 min using an electric heating plate equipped with a temperature control couple (Figure S1). The values obtained by this method have been previously verified with different supramolecular gels by means of DSC measurements as well as the inverse flow method (IFM)³. It should be noted that the values determined by IFM strongly depend on factors such as cooling rate, aging time, thermal history, and degree of hysteresis among others. Moreover, verification of the independence of the position inside the custom made apparatus has also been carried out.⁴ Herein, the temperature at which the gel started to break was defined as T_{gel} with an estimated error of ± 2 °C after several heating-cooling cycles.

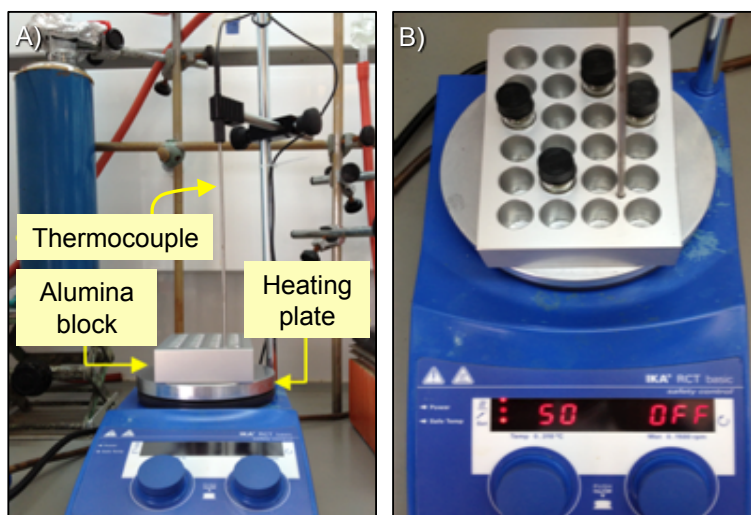


Fig. S1 Custom made apparatus for T_{gel} determinations. A) Front view of the set-up. B) Top view of the set-up during a typical experiment. The vials must fit smoothly inside the molds to ensure the optimal transmission of the heat flow. T_{gel} of undoped gel made of **G-1** (48 ± 2 °C) remained invariable after doping and after irradiation.

2.2. Oscillatory rheology: Oscillatory rheology was performed with an AR 2000 Advanced rheometer (TA Instruments) equipped with a Julabo C cooling system. A 1000 μm gap setting and a torque setting of 40,000 dynes/cm² at 25 °C were used for the measurements in a plain-plate (40 mm, stainless steel). The following experiments were performed using 2 mL total gel volume: a) Dynamic strain sweep (DSS): variation of G' and G'' with strain (from 0.01 to 100%); b) dynamic frequency sweep (DFS): variation of G' and G'' with frequency (from 0.1 to 10 Hz at 0.1% strain); c) dynamic time sweep (DTS): variation of G' and G'' with time keeping the strain and frequency values constant and within the linear viscoelastic regime as determined by DSS and DFS measurements (strain = 0.1% strain; frequency = 1 Hz). Figure S2 displays typical rheological plots for the undoped gel made of **G-1** ($c = 10 \text{ g L}^{-1}$) and the doped gel as described in Table 1 (entry 2) before and after 2 h irradiation with a pulsed laser at $\lambda_{\text{exc}} = 532 \text{ nm}$.

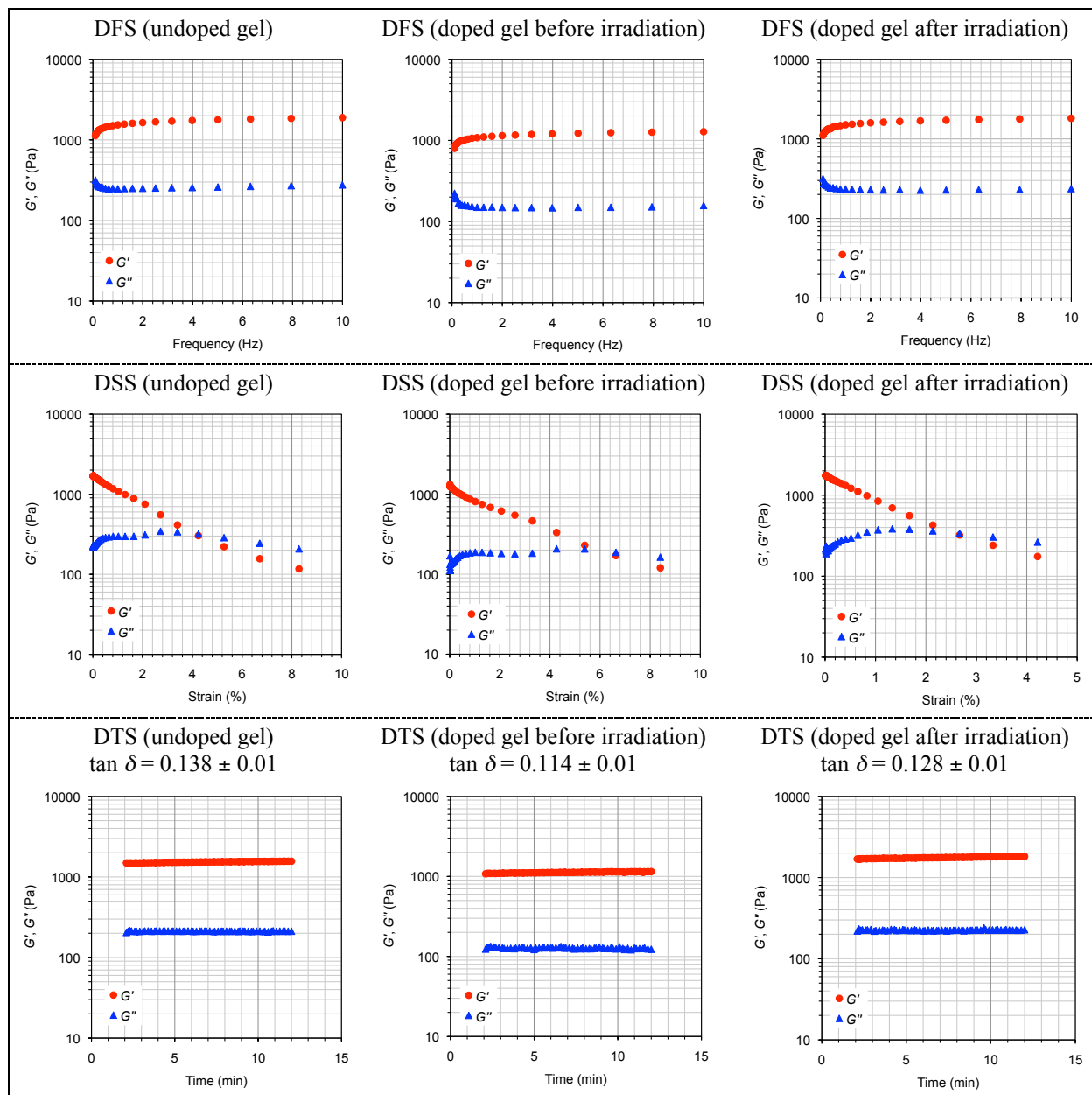


Fig. S2 Oscillatory rheological experiments of model undoped and doped gels. Conditions for preparing the doped gel: $[\text{G-1}] = 10 \text{ g L}^{-1}$, $[\text{I}] = 10 \text{ mM}$, $[\text{PtOEP}] = 33 \text{ }\mu\text{M}$, $[\text{DPA}] = 6.7 \text{ mM}$.

2.3. General procedure for steady-state irradiations: The corresponding doped gel was irradiated under aerobic conditions during 120 min in a pulsed Nd:YAG-laser instrument using 532 nm as selective wavelength. Afterwards, dichloromethane (5 mL) was added and washed with brine (5 mL). The organic phase was separated, dried (Na_2SO_4) and filtered for further analysis. GC/FID (7820A Agilent) was used to follow the course of the reaction and determining conversions and total yields (see section 2.4).

2.4. GC/FID: GC was calibrated using a four-point calibration vs. 10 mM of the internal standard *n*-pentadecane (Std.). Representative calibration curves and GC chromatograms are shown in Figure S3 and Figures S4-S7, respectively. The GC oven temperature program was adjusted as follows: The initial temperature (50 °C) was kept for 0.5 min, and subsequently increased at a rate of 25 °C min^{-1} over a period of 8 min until the final temperature (280 °C) was reached and maintained for 10 min.

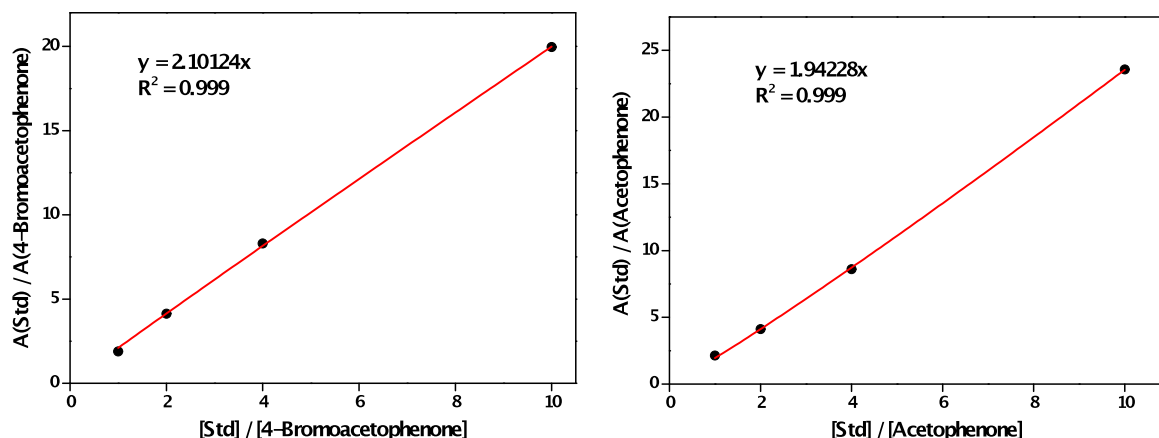


Fig. S3 Quantitative GC calibration for substrate **ArBr** conversion and product **ArH** formation vs. 10 mM of internal standard (Std.) *n*-pentadecane.

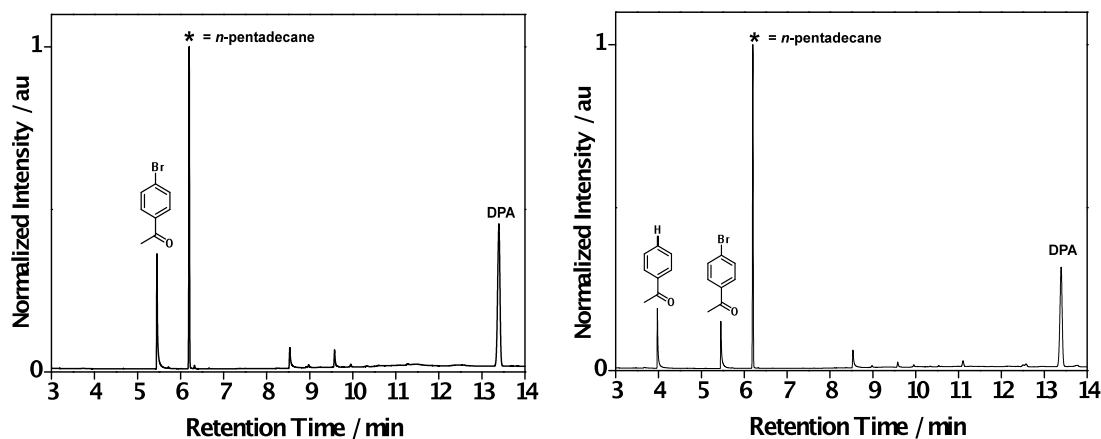


Fig. S4 Representative normalized GC/FID chromatograms for the **INTRAGEL** photoreduction of **1** in the presence of the TTA system (**PtOEP** + **DPA**) in the gel made from **G-1** (DMF) obtained before (*left*) and after 2 h of pulsed laser irradiation at 532 nm (*right*).

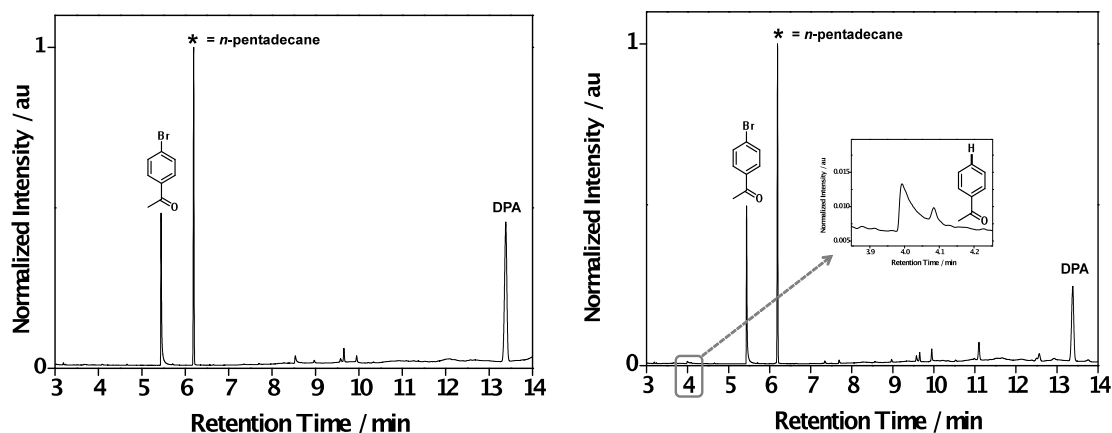
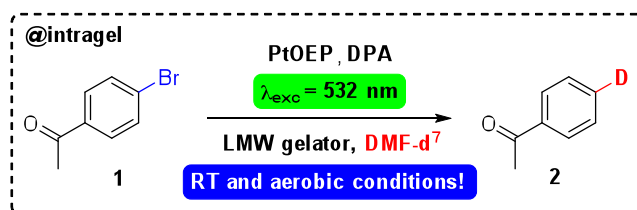


Fig. S5 Representative normalized GC/FID chromatograms for the photoreduction of **1** in the presence of the TTA system (**PtOEP** + **DPA**) in aerated DMF solution obtained before (*left*) and after 2 h of pulsed laser irradiation at 532 nm (*right*).



Conversion = 47%; MB = 91%; Yield = 35%

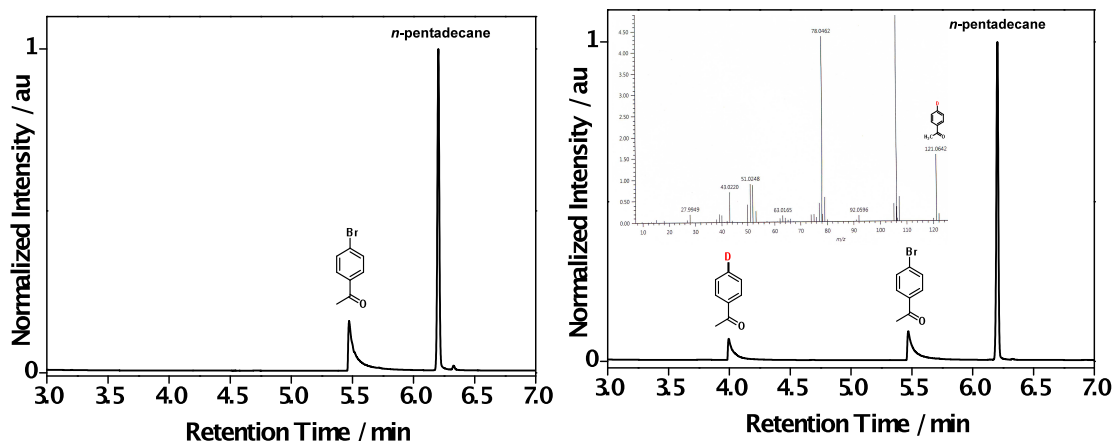


Fig. S6 Representative normalized GC/FID chromatograms for the **INTRAGEL** photoreduction of **1** in the presence of the TTA system (**PtOEP** + **DPA**) in the gel made from **G-1** (DMF-d⁷) obtained before (*left*) and after 2 h of pulsed laser irradiation at 532 nm (*right*). Inset: ESI-MS spectrum of formed deuterated acetophenone: Exact mass (EI⁺) required for C₈H₇OD 121.06479 (M⁺); found 121.06422.

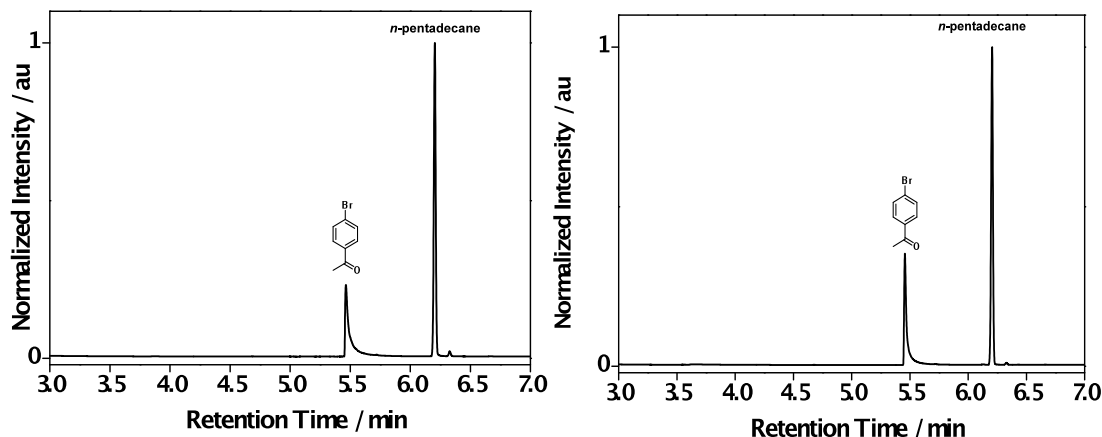


Fig. S7 Representative normalized GC/FID chromatograms for the **INTRAGEL** photoreduction of **1** in the presence of the TTA system (**PtOEP** + **DPA**) in the gel made from **G-1** (toluene) obtained before (*left*) and after 2 h of pulsed laser irradiation at 532 nm (*right*).

2.5. UV-vis and fluorescence spectroscopy: UV-vis analyses were performed on a Varian Cary 50 UV-vis spectrophotometer. Steady-state fluorescence measurements were performed with Horiba FluoroMax-4 fluorimeter. Excitation and emission slit widths were 1 nm. Screw-cap Hellma quartz SUPRASIL® cuvettes (117.100F-QS, 10 × 10 mm) with screw cap with PTFE-coated silicon septum were used. **DPA** concentration was 0.01 mM in DMF. Figure S8 shows the interception point between absorption and emission bands of **DPA** for the determination of excited singlet state energy.

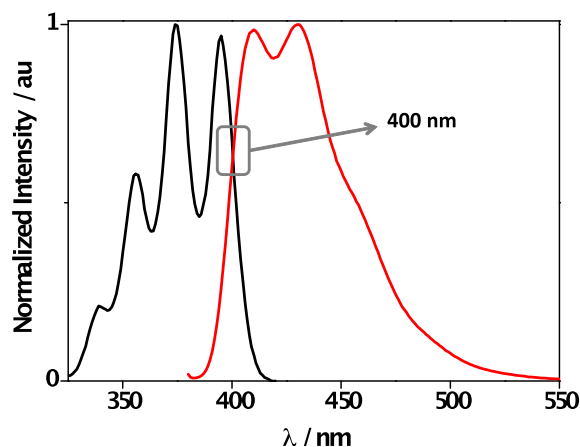


Fig. S8 Normalized absorption (black) and emission (red, $\lambda_{\text{exc}} = 375$ nm) of an aerated DMF solution of **DPA** (0.01 mM). Singlet energy of **DPA** in DMF, $E_s = 71.5$ kcal mol⁻¹.

2.6. Cyclic voltammetry: The redox potentials were measured by cyclic voltammetry with an Autolab PGSTAT302N Metrohm apparatus. All measurements were made in deaerated DMF containing tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte, a glassy carbon as working electrode, a platinum wire as counter electrode, a silver wire as pseudo reference and ferrocene as internal standard. The scan rate was 0.05 V s⁻¹. Potentials are reported with respect to the saturated calomel electrode (SCE) as reference (Figure S9).⁵ Figure S10 shows the reduction potentials of selected aryl bromides and free energy changes (ΔG_{ET}) of the electron transfer process.

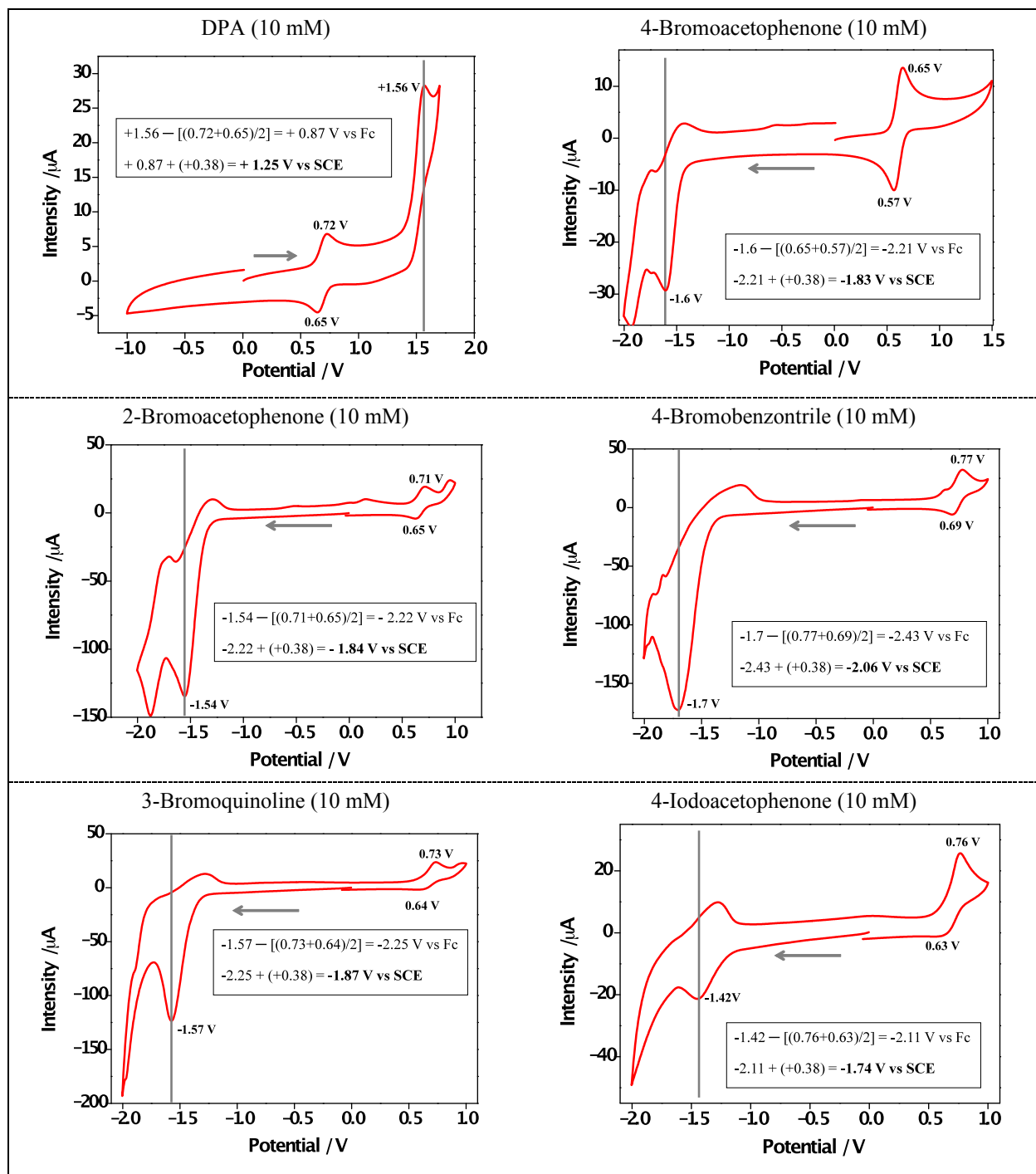


Fig. S9 Cyclic voltammetry of DPA and substrates in deaerated DMF.

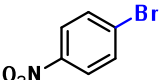
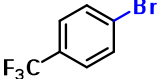
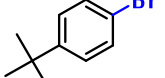
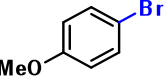
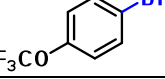
Aryl Bromides	E_{red}	$\Delta G_{\text{ET}} (S_1)$
	-2.07	+5.06
	-2.42	+13.13
	-2.93	+24.89
	-2.84	+22.81
	-2.66	+18.66

Fig. S10 Reduction potentials of selected aryl bromides and free energy changes (ΔG_{ET}) of the electron transfer process. $\Delta G_{\text{ET}} (\text{kcal mol}^{-1}) = 23.06 \times [E_{\text{ox}} - E_{\text{red}} + (2.6/\epsilon) - 0.13] - E^*(S_1)$.

2.7. Laser flash photolysis system: The pump source is an optical parametric oscillator (OPO) pumped by the third Harmonic of a Nd:YAG-laser (Surelite II and Surelite OPO PLUS, Continuum). The wavelength can be set from 400 nm to ca. 700 nm, with a pulse width of ca. 5 ns. The typical pulse duration is 8 ns.

2.8. LED photolysis system: The vial containing the corresponding doped gel was placed vertically above the aperture of the LED during the experiments using a custom made cooling apparatus as shown in Figure S11.

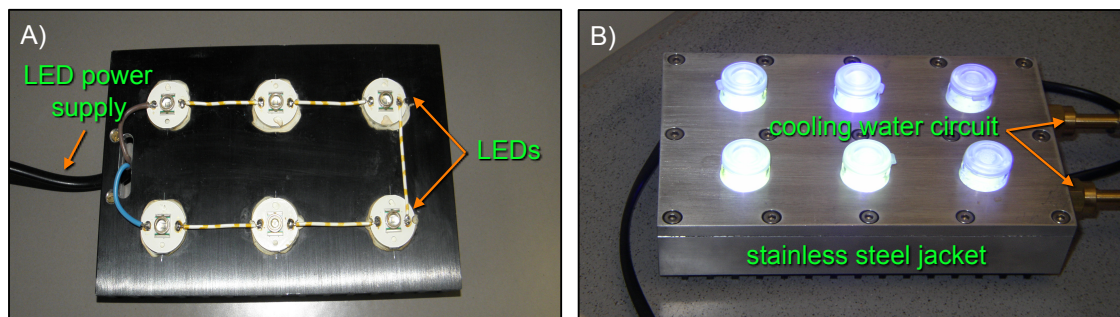


Fig. S11 Typical custom made cooling apparatus with an array of LEDs used in our lab: A) array of six LEDs connected in series to a power supply. B) Set-up during irradiation with a stainless steel jacket to facilitate refrigeration of the vials. The distance between the LEDs and the reaction vials is adjusted to 0.9 ± 0.1 cm.

3. References

- 1 Y. G. Yi, T. Y. Wang and M. H. Liu, *Soft Matter*, 2007, **3**, 1312-1317.
- 2 K. Hanabusa, M. Yamada, M. Kimura and H. Shirai, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 1949-1951.
- 3 J. E. Eldrige and J. D. Ferry, *J. Phys. Chem.*, 1954, **58**, 992-995.
- 4 J. Bachl, A. Hohenleutner, B. B. Dhar, C. Cativiela, U. Maitra, B. König, D. D. Díaz, *J. Mater. Chem. A*, 2013, **1**, 4577-4588.
- 5 V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, 2000, **298**, 97-102.